tassium iodide solution. The orange-red, liquid product of the decomposition was purified by distillation. One fraction, amounting to a yield of about 20%, had b.p. 80° (17 mm.), $n^{20}D$ 1.610 and d^{20}_4 1.23. These properties when compared with those previously reported[3] identify the compound as benzenesulfenyl chloride.

Hydrolysis of Sulfur Trichlorides.—When added to a cold sodium bicarbonate solution ethylsulfur trichloride formed sodium ethanesulfinate which reacted on boiling with benzyl chloride to form benzyl ethyl sulfone. The latter melted at 84° and the melting point was unchanged when the sample was mixed with benzyl ethyl sulfone prepared by the oxidation of benzyl ethyl sulfide.

Unsuccessful Attempts to Prepare Sulfur Trichlorides.—Benzyl disulfide (5 g.) was chlorinated at −40°, but no precipitate formed. The reaction mixture was distilled under reduced pressure and there was obtained 2 g. of liquid with the properties: b.p. 89° (37 mm.), $n^{20}D$ 1.540, d^{20}_4 1.11, which identify the product as benzyl chloride.

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The Structure of Isoamidone. I

BY NELSON R. EASTON, SAMUEL J. NELSON[1] AND VELMER B. FISH

While carrying out some work on 4,4-diphenyl-6-dimethylamino-3-hexanone we had occasion to prepare several derivatives. The melting points of these compounds agreed very closely with those reported[2] for Isoamidone I, and the melting points of the hydrochloride of this substance, when taken in the same melting point apparatus was the same as that of the hydrochloride of 4,4-diphenyl-6-dimethylamino-3-hexanone. No depression in melting points was observed on mixing.

These data prove that Isoamidone I is 4,4-diphenyl-6-dimethylamino-3-hexanone. A logical explanation for the finding of this compound in the mother liquors from the synthesis of Amidone is that the propylene chlorohydrin, which was used in the preparation of the dimethylaminochloropropane, was contaminated with ethylene chlorohydrin.

Experimental

The 6-dimethylamino-4,4-diphenyl-3-hexanone was prepared by the procedure[3] of Dupre, *et al.*, in which 4-bromo-2,2-diphenylbutanenitrile is aminated with dimethylamine and then the ketone is prepared by the usual Grignard reaction. The ketone was usually isolated as the hydrobromide and then converted to the desired derivative.

Preparation of Derivatives of 6-Dimethylamino-4,4-diphenyl-3-hexanone.—The hydrobromide was dissolved in warm water and the solution was made basic with sodium hydroxide. The oil was extracted with ether and the ether was dried over magnesium sulfate and the solvent distilled. Concentrated hydrochloric acid and ethanol were added. The mixture was concentrated to dryness and crystallized on scratching. It was recrystallized from acetone and melted at 173.5–175°,[4] not depressed on an admixture of Isoamidone I hydrochloride of m.p. 173.5–175°.

Anal. Calcd. for $C_{20}H_{26}NOCl$: Cl, 10.68. Found: Cl, 10.92.

Methiodide (from absolute ethanol), m.p. 199.5–200.5°; reported for Isoamidone I methiodide[2] 195–196°.

(1) University of Chicago, Chicago, Ill.

(2) N. R. Easton, J. H. Gardner and J. R. Stevens, THIS JOURNAL, **70**, 76 (1948).

(3) D. J. Dupre, J. Elks, B. A. Hems, K. N. Speyer and R. M. Evans, *J. Chem. Soc.*, 500 (1949).

(4) M. Bockmühl and S. Ehrhart, *Ann.*, **561**, 52 (1948), list 173–175°.

Anal. Calcd. for $C_{21}H_{26}NOI$: N, 3.20. Found: N, 3.17, 3.10.

Oxalate (from absolute ethanol), m.p. 161.5–163°; reported for Isoamidone I oxalate,[2] 158–160°.

Anal. Calcd. for $C_{20}H_{25}NO \cdot C_2H_2O_4$: N, 3.65. Found: N, 3.60.

Picrate (from ethanol) m.p. 134–136°; reported for Isoamidone I picrate,[2] 131–133°.

Anal. Calcd. for $C_{26}H_{28}N_4O_8$: N, 10.68. Found: N, 10.48, 10.52.

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The Rate of the Reaction between Thallium(III) and Iron(II) in Perchloric Acid Solution

BY OTTO L. FORCHHEIMER[1] AND ROBERT P. EPPLE

While preparing a paper describing our work[2] on the kinetics of the Fe(II)–Tl(III) reaction, the article by Johnson[3] on the same subject appeared. We are therefore limiting our report to results which amplify or supplement those reported by him. Measurements made under the same conditions agree quantitatively.

Experimental

The preparation of the thallous, thallic, ferrous and ferric perchlorates has been previously described.[4] The perchloric acid was G. F. Smith Chemical Company's 70% "purified." Spot tests as recommended by Feigl[5] showed that this acid had a ferric ion content of less than $3 \times 10^{-6}F$ and a chloride ion concentration of less than 3×10^{-5}. No chlorate could be detected. The ferrous perchlorate stock solution contained traces of chloride ion (for quantitative information see reference 4), but not in sufficient amounts to affect the results of this investigation. Sodium and lithium perchlorates were prepared by adding the reagent grade carbonate to perchloric acid. Basic magnesium carbonate was used in the same manner to prepare a magnesium perchlorate solution. Manganese perchlorate solutions were prepared by dissolving the reagent grade metal in perchloric acid. These solutions all contained less than the above limits of iron and chloride ion. All other chemicals used were Baker and Adamson reagent grade.

The reactants, in separate glass-stoppered bottles, were allowed to come to uniform temperature in a constant temperature bath. The order of addition did not affect the results. All experiments were carried out at $25 \pm 0.1°$. The time of starting a run was taken at the time when one half of the second reagent had been added to the first. Samples for analysis were taken with a pipet and discharged into an acidic chromate solution which stopped the reaction by oxidizing iron(II) and precipitating thallium(I). The acidic precipitate was metathesized into the stoichiometric thallous chromate by a previously described method.[4]

Although chloride ion has been mentioned as a catalyst for the dichromate oxidation of thallium(I),[6] tests showed

(1) University of Chicago, Chicago, Ill.

(2) O. L. Forchheimer, Thesis, Brown University, 1951.

(3) C. E. Johnson, Jr., THIS JOURNAL, **74**, 959 (1952).

(4) O. L. Forchheimer and R. P. Epple, *Anal. Chem.*, **23**, 1445 (1951).

(5) F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., Inc., New York, N. Y., 1939, pp. 97–98, 161.

(6) P. A. Shaffer, *Cold Spring Harbor Symposia Quant. Biol.*, **7**, 50 (1939).

that this analytical method gave good results in the presence of the chloride ion concentrations used in this study.

Results

The specific rate, k, is obtained from the integrated rate expression

$$k = \frac{1}{t(a - 2b)} \, 2.3 \log \frac{b(a - 2x)}{a(b - x)}$$

where t designates the time of reaction, a the initial concentration of the iron(II), b the initial concentration of thallium(III) and x the experimentally determined amount of thallium(I) formed. k has been calculated and listed for all experiments except those in the presence of added chloride ion where the above equation does not apply.

The specific rate was observed to decrease slightly after the reaction was 50–70% complete. In the absence of oxygen this decrease was not observed. Since the effect of oxygen was small, no effort was made to exclude it. The reported rate constants are the averaged rate constants of the first 50–60% of the reaction.

The results of the analytical work in reference 5 indicate that x is subject to a probable error of 0.27 mg. and to a maximum error of 0.7 mg. Differentiating k partially with respect to x we obtain a probable error for k of 0.015 liter-F.W.$^{-1}$-minute^{-1}. This amounts to a probable error of 2–3% of the k values obtained in this study.

In Table I are listed some representative results obtained at an acid concentration of 2.0 F. Run 11 demonstrates that the products do not affect the rate. In the various experiments k was shown to be constant over a four-fold concentration range in thallium(III) and a three-fold variation in the concentration of iron(II). This variation is slightly greater than that studied by Johnson,[3] and the experiments as a whole were conducted at higher concentrations than he used, extending the concentration ranges over which this reaction has been found to be second order. The nature of the analytical method limited the concentration range investigated here. The magnitude of k found here at an ionic strength of 2 cannot be directly compared with the results of Johnson at an ionic strength of 3.

TABLE I

SOME RESULTS AT 2.0 F PERCHLORIC ACID CONCENTRATION

Run	a, F	b, F	$[Fe(ClO_4)_3]$, F	$[TlClO_4]$, F	k, F.W.$^{-1}$ liter^{-1} minute^{-1}
6	0.0201	0.0083	.....	.....	0.69
7	.00715	.00342	.....	.....	.67
8	.0262	.0128	.....	.....	.72
11	.00715	.00342	0.00767	0.00301	.67

Figure 1 illustrates the effect of chloride ion as an inhibitor. This effect is similar to the action of chloride ion on the rate of the electron exchange between thallium(I) and thallium(III) studied by Harbottle and Dodson.[7] They found that chloride ion in small concentrations decreased the rate of the exchange enormously. The conditions prevailing in run 20 are similar to those in a solution
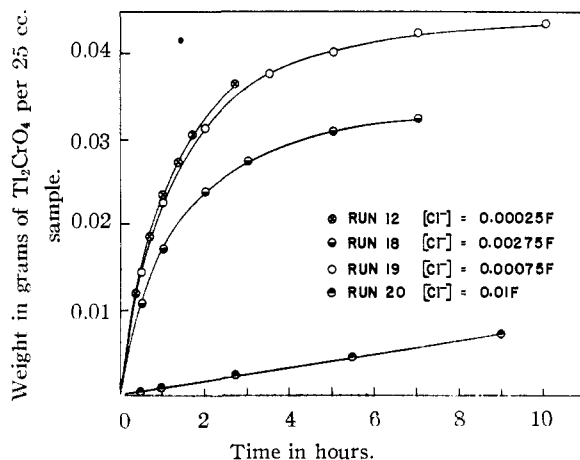
(7) G. Harbottle and R. W. Dodson, THIS JOURNAL, **73**, 2442 (1951).

Fig. 1.—The effect of chloride ion on the rate $a = 0.0201$, $b = 0.0075$, $HClO_4 = 1.5 \ F$.

for which Harbottle and Dodson found that thallium(III) moved toward the cathode carrying chloride with it, and observed no chloride ion moving toward the anode. This shows that under such conditions (the concentrations of thallium(III) and chloride ion being essentially equivalent) the thallium(III) is capable of complexing all the chloride present. Benoit[8] reports a dissociation constant of $10^{-8.1}$ for $TlCl^{++}$. Silverman and Dodson report that chloride ion catalyzes the iron (II)–iron(III) exchange reaction.[9] It is very probable then that we are dealing with a reaction between iron(II) and a monochlorothallate or perhaps a dichlorothallate ion. The rates obtained when chloride less than equivalent to the thallium(III) concentration was present (runs 18 and 19) approximate the second order rate expected if the thallium(III) concentration is replaced by the quantity $([Tl(III)]-[Cl^-])$. However, the rate was somewhat faster than calculated using this "reduced concentration" and the chloro complexes must account for a fraction of the reaction.

The effect of varying the concentration of perchloric acid is shown in Fig. 2. The ionic strength was not kept constant in this series of runs and is essentially equivalent to the acid concentration. At acid concentrations between 0.75 and 1.5 F the rate of the reaction decreases with increasing acid concentration, illustrating the important part which hydrolyzed species play in the reaction, as
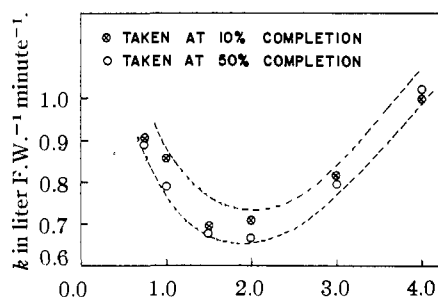

Fig. 2.—Variation of rate with acid concentration.

(8) R. Benoit, Soc. Chim. France, **5–6**, 518 (1949).

(9) J. Silverman and R. W. Dodson, J. Phys. Chem., **56**, 846 (1952).

quantitatively shown by Johnson.[3] Between 2.0 and 4.0 F, the rate of the reaction increases with increasing acid concentration, due, perhaps, to a kinetic salt effect, or perhaps the perchlorate ion concentration itself has a positive effect on the reaction due to ion pair formation.[10] Attempts were made to study the reaction at lower acid concentrations, but the hydrolysis of the thallium(III) solutions interfered.[11]

A direct comparison is afforded with Johnson's results by the run in 3.0 F HClO$_4$. The experimentally obtained value of k is 0.77. Using Johnson's formula,[3] applicable at an ionic strength of 3, we get $k = 0.74$.
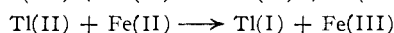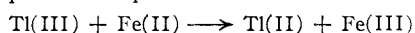
The results of some runs in the presence of certain cations are listed in Table II. The experiment in the presence of a small quantity of manganese was performed in order to see whether the presence of this ion could provide an alternative reaction path to the system. Shaffer[12] has shown manganese(II) to be a good catalyst for some reactions between two-electron reagents and one-electron reagents, as it can form oxidation states of 2, 3 and 4 in solution. No catalytic effect was found in this system. The other salts increased the rate, as was expected, in view of the results obtained at high acid concentrations. These results are, however, insufficient to draw any conclusions about the effect of ionic strength, perchlorate ion concentration or any specific ionic effect.

TABLE II

EFFECT OF SOME CATIONS ON THE RATE

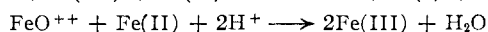$b = 0.0113$, $a = 0.0201$, [HClO$_4$] = 1.5 F

Run	Added salt and its concentration	k
13	None	0.67
21	0.50 F LiClO$_4$	.81
22[a]	.011 F Mn(ClO$_4$)$_2$	.68
23	.20 F Mg(ClO$_4$)$_2$	.83
24	.50 F NaClO$_4$	.87

[a] Acid concentration in this run 1.79 F.

One can account for the kinetics of the reaction by a simple two-step mechanism

$$Tl(III) + Fe(II) \longrightarrow Tl(II) + Fe(III)$$
$$Tl(II) + Fe(II) \longrightarrow Tl(I) + Fe(III)$$

or alternatively

$$H_2O + Tl(III) + Fe(II) \longrightarrow FeO^{++} + Tl(I) + 2H^+$$
$$FeO^{++} + Fe(II) + 2H^+ \longrightarrow 2Fe(III) + H_2O$$

where the first step in each case is the slow, rate-determining reaction. Since the specific rate is independent of the concentrations of the reactants (over the range studied) and also independent of the concentration of the products, no measurable equilibrium can be involved in the first step. On the basis of the kinetics no choice can be made between iron(IV) and thallium(II) as an intermediate. However, the path through thallium(II)

(10) Cf. A. R. Olsen and T. R. Simonsen, J. Chem. Phys., 17, 1167 (1949).

(11) Thallic hydroxide precipitates only slowly from solutions when the solubility product is not greatly exceeded. The solubility product of Tl(OH)$_3$ was found to be 8.8×10^{-44} by letting a small excess of Tl(OH)$_3$ precipitate from a 0.5 F perchloric acid solution. This value is in good agreement with the value 1.5×10^{-44} calculated by Sherrill and Haas (THIS JOURNAL, 58, 952 (1936)).

(12) P. A. Shaffer, ibid., 55, 2169 (1933).

is preferred because an intermediate which can act as a reducing agent is necessary to explain the induced oxidation by oxygen.

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Improvements in the Preparation of Melibiose from Raffinose. A New Form of Melibiose

BY HEWITT G. FLETCHER, JR., AND HARRY W. DIEHL

The preparation of the disaccharide melibiose by the fermentative hydrolysis of the trisaccharide raffinose was developed by Hudson and Harding[1-3] and has, in the past, uniformly yielded the well-known β-melibiose dihydrate melting at about 85 to 86°[4] and mutarotating in water $[\alpha]^{20}$D $+123.5°$ $\rightarrow +143.1°$ (anhydrous basis, c 4). Attempts to obtain melibiose in other modifications have failed although Loiseau[5] reported that dehydration of β-melibiose dihydrate afforded a form, probably amorphous, which showed a slight levomutarotation.[6]

Recently we were furnished with a sample of material[7] derived from raffinose by the Hudson–Harding procedure.[1-3] In sharp contrast to previous samples this melted at 179–181°.[8] Elementary analysis and loss of weight at 100° in vacuo gave values corresponding to a disaccharide containing 0.85 mole water. Acetylation with acetic anhydride and sodium acetate afforded β-melibiose octaacetate in high yield. On an anhydrous basis the substance mutarotated $[\alpha]^{20}$D $+166.0° \rightarrow +142.3°$ (c 4) in water; the first-order reaction constant, 0.0090 (min., decimal logs) is close to that (0.0088) reported by Hudson and Yanovsky[9] for melibiose. Recrystallization from aqueous alcohol gave the melibiose in crystalline form containing one or slightly less than one mole of water. From methanol the sugar was obtained in anhydrous form which, upon standing in the air, approached the monohydrate in composition. Regardless of state of hydration, the recrystallized material showed on an anhydrous basis the above rotational constants and was therefore pure melibiose.

Solutions of either β-melibiose or of the new form of melibiose could be induced to crystallize in either form by appropriate seeding. However, the new form, less soluble and a better crystallizer, was

(1) C. S. Hudson and T. S. Harding, THIS JOURNAL, 37, 2734 (1915).

(2) T. S. Harding, Sugar, 25, 514 (1923).

(3) F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 473.

(4) Melting points cited are corrected for stem exposure.

(5) D. Loiseau, Z. Ver. deut. Zucker-Ind., 40, 1050 (1903).

(6) The terms levomutarotation and dextromutarotation are used here to denote rotatory changes in the negative and positive directions, respectively.

(7) We wish to thank Mr. Robert S. Black of the Pfanstiehl Chemical Company for the donation of this sample.

(8) This value varied with the rate of heating; very slow heating afforded a value of 185–188°.

(9) C. S. Hudson and E. Yanovsky, THIS JOURNAL, 39, 1013 (1917).