

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

Comparison of Metallic Chlorides as Catalysts for the Friedel-Crafts Ketone Synthesis^{1,2}

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Although aluminum chloride is ordinarily the catalyst chosen for the Friedel-Crafts ketone synthesis, occasional use is made of other metallic chlorides.³ The only work dealing with quantitative comparisons, however, has been confined to examining mixed catalysts.^{4a,b,c,d}

If the Friedel-Crafts ketone synthesis were uncomplicated by side reactions and consecutive reactions, a comparison of catalysts could mean only a comparison of rates of reaction, such as has been made for both the hydrocarbon and the ketone synthesis.⁵ Since in practice the maximum yields obtainable with different catalysts vary widely, these measures of the extent of the reaction constitute the usual basis of comparison. In the exploratory work here reported, we chose to measure yields of *p*-methylacetophenone from acetyl chloride, toluene⁶ and various catalysts. Both concentration of catalysts and time of reaction were varied separately until optimum conditions, as indicated by maximum yield, were attained for each catalyst.

For measuring the yield of ketone, we originally used the hydroxylamine hydrochloride method of Bryant and Smith.⁷ However, we found the end-point of the acidimetric titration so exceedingly blurred by pyridine (which Bryant and Smith added to complete oxime formation) that we now prefer the older procedure of Bennett and Cocking,⁸ in which the hydrochloric acid liberated from

hydroxylamine hydrochloride is titrated at intervals until a permanent end-point is reached. Our principal improvement in this method is a sharpening of the end-point (indicator, butter yellow) by using absolute methanol instead of 95% ethanol as reaction medium.

Figures 1 and 2 present most of our data. Certain chlorides gave no ketone: antimony trichloride, arsenic trichloride,⁹ boron trichloride, cadmium chloride, calcium chloride, chromic chloride, cobaltous chloride, cupric chloride, cuprous

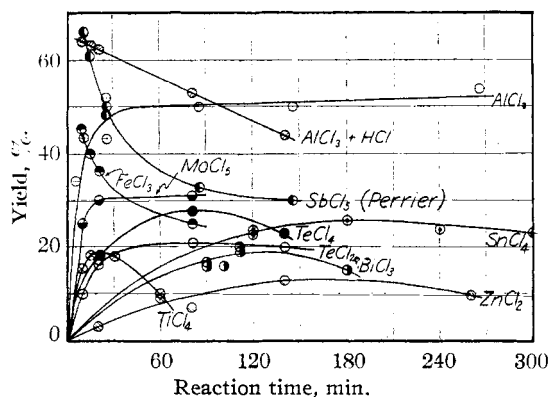


Fig. 1.—Variation of yield of *p*-methylacetophenone with reaction time.

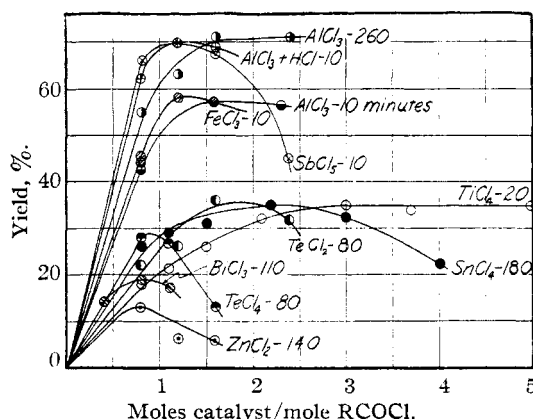


Fig. 2.—Variation of yield of *p*-methylacetophenone with amount of catalyst (numbers following formulas indicate reaction times).

(1) Most of this paper is based upon theses submitted by David M. Wilson and F. M. Johnson in partial fulfillment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1937 and 1940, respectively.

(2) Presented before the Division of Organic Chemistry at the Cincinnati meeting of the American Chemical Society, April, 1940.

(3) For a partial list of references see Calloway, *Chem. Rev.*, **17**, 327 (1935).

(4) (a) Gallay and Whitby, *Can. J. Research*, **2**, 31 (1930); (b) Riddell and Noller, *This Journal*, **52**, 4365 (1930); **54**, 290 (1932); (c) Groggins and Nagel, *Ind. Eng. Chem.*, **26**, 1313 (1934); (d) Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill Book Company, Inc., New York, N. Y., 2d ed., 1938, pp. 662-663.

(5) Martin, Pizzolato and McWaters, *This Journal*, **57**, 2584 (1935); Ulich and Heyne, *Z. Elektrochem.*, **41**, 509 (1935).

(6) Anisole was originally tried as the aromatic reagent and solvent, in the hope of magnifying the activity of feeble catalysts, but its reactivity proved so great that about 30% yields of *p*-methoxyacetophenone were obtainable by refluxing it with acetyl chloride without any catalyst at all. Toluene was thereupon chosen in preference to benzene by the same reasoning.

(7) Bryant and Smith, *This Journal*, **57**, 57 (1935).

(8) Bennett and Cocking, *Analyst*, **56**, 79 (1931).

(9) This contradicts the apparently unsupported statement of Moelwyn-Hughes and Sherman (*J. Chem. Soc.* 108 (1936)) that arsenic trichloride, among others, catalyzes the reaction of an acid chloride with aromatic hydrocarbons.

chloride, ferrous chloride, germanium tetrachloride, iodine trichloride, lanthanum trichloride, lead dichloride, magnesium chloride, manganese dichloride, mercuric chloride, nickelous chloride, phosphorus pentachloride, phosphorus trichloride, selenium monochloride, silicon tetrachloride, sodium chloride, stannous chloride, sulfur monochloride, thallos chloride and thorium tetrachloride.

Comparison of Catalysts.—Most of the hitherto untested compounds found ineffective would have been predicted to be so, but this is not true of such borderline ones as the chlorides of boron, arsenic, magnesium and germanium, and stannous chloride. It is possible that some of these, like antimony trichloride, become active only at temperatures higher than any we used. Lead tetrachloride has given evidence of a small catalytic activity, but the principal reaction is chlorination of the toluene. For the same reason, antimony pentachloride, if added to the toluene first, produces only a 2% yield of ketone.

The order of decreasing efficiency of catalysts studied in this work is AlCl_3 , SbCl_5 , FeCl_3 , TeCl_2 , SnCl_4 , TiCl_4 , TeCl_4 , BiCl_3 , ZnCl_2 . This order differs from that given by Calloway³ only in the position of zinc chloride. The superiority of tellurium dichloride over tellurium tetrachloride is surprising, for the lower chloride of a metal is generally too much more salt-like to be effective. It is difficult to correlate activities of catalysts with positions of the metals in the ordinary forms of the periodic table; the "oxide periodicity pattern" on the spiral table of Irwin¹⁰ groups more Friedel-Crafts catalysts together than any other arrangement we have seen.

Individual Catalysts.—The fallacy in refluxing Friedel-Crafts reaction mixtures as long as hydrogen chloride is evolved has been pointed out,¹¹ but there seems to be no other literature record of marked decrease in yield with increased reaction time. This effect is shown by reactions involving aluminum chloride activated by hydrogen chloride, antimony pentachloride, ferric chloride and titanium tetrachloride; its cause is probably the self-condensation of the ketone demonstrated by Calloway.¹¹ Chemically pure aluminum chloride produces no decrease in yield within two to three hours. Such difference in catalytic effect of slightly different samples of aluminum chloride has often been noted before.

(10) Irwin, *J. Chem. Education*, **16**, 335 (1939).

(11) Calloway and Green, *THIS JOURNAL*, **59**, 809 (1937).

The proportionality of yield to the ratio moles of catalyst/moles of acid chloride for values of the ratio up to and including one has been demonstrated too often to need more confirmation, at least for aluminum chloride. However, Riddell and Noller^{1b} say of aluminum chloride and ferric chloride: "A point that does not seem to have been previously recorded is that the yield rapidly falls off when more than these optimum amounts [1:1] are used." This is not true of any of our catalysts except antimony pentachloride and tellurium tetrachloride, though excess zinc chloride and bismuth trichloride seem to have a small deleterious effect.

Experimental

Materials.—C. P. toluene and acetyl chloride were used without further purification, the latter being stored in small glass-stoppered bottles in a desiccator.

Anhydrous ferric chloride, boron trichloride, tellurium tetrachloride and molybdenum pentachloride were made by chlorinating the element and redistilling or resubliming the product. Commercial anhydrous zinc chloride was either fused or distilled to remove traces of water. Ferrous chloride, magnesium chloride and aluminum chloride were made by heating the powdered metals in a current of dry hydrogen chloride; the adsorbed gas activated the aluminum chloride so obtained. Anhydrous stannous chloride, cadmium chloride and cupric chloride were prepared by warming the hydrated salts with acetic anhydride, as recommended by Stephen¹² for the tin compound. The products were analyzed for chlorine to make sure they were acceptable. The method fails to give pure anhydrous chlorides of nickel and manganese. Distilled stannous chloride also was tested.

Barium chloride was made simply by heating the dihydrate, but lanthanum chloride required the special vacuum dehydration described by Kleinheksel and Kremers.¹³ Tellurium dichloride and antimony trichloride were made by refluxing tellurium tetrachloride and antimony pentachloride, respectively, with an excess of the corresponding metals, and then distilling out the reduction products. Selenium monochloride was obtained by the method of Lenher and Kao.¹⁴

Stannic chloride, antimony pentachloride and bismuth trichloride were purified by distilling the c. p. reagents before use. Lead tetrachloride was obtained and used without complete purification, by treating pyridinium hexachloroplumbate with concentrated sulfuric acid. Germanium tetrachloride was kindly loaned by Dr. Warren C. Johnson of the University of Chicago. All catalysts not otherwise mentioned were c. p. reagents, used without purification.

Procedure.—In studying a particular catalyst, the amount of it was first kept constant while the heating time was varied until the optimum was found; then variation in amounts was tested for its effect at this optimum time.

(12) Stephen, *J. Chem. Soc.*, 2786 (1930).

(13) Kleinheksel with Kremers, *THIS JOURNAL*, **50**, 959 (1928).

(14) Lenher and Kao, *ibid.*, **47**, 772 (1925).

In the standard procedure,¹⁵ 10 ml. of toluene is pipetted into a dry 250-ml. flask which can be fitted to either a reflux condenser or a distillation condenser by an interchangeable ground glass joint. Exactly 1 ml. of acetyl chloride is added by means of a calibrated pipet. The selected amount of catalyst (powdered, if solid) is then added all at once, suitable precautions having been taken to minimize hydrolysis during its measurement. Timing is begun from the first visible sign of reaction, usually bubbling; this may or may not require preliminary heating. During the reaction a further 5 ml. of toluene is dripped down through a loose plug of glass wool midway in the reflux condenser, to scrub acetyl chloride vapor from the escaping hydrogen chloride. As soon as any vigorous reaction subsides the flask is heated in boiling water and in some cases with a free flame afterward; for estimating reaction times, the time of refluxing over a flame (at about 110°) is doubled and added to time of heating in the water-bath.

After whatever time of reaction chosen is complete, the flask is quickly cooled and its contents hydrolyzed by adding cold water through the condenser. The reaction mixture is made just alkaline to phenolphthalein, diluted to about 150 ml., and distilled into a separatory funnel until at least 75 ml. of distillate have been collected, the last droplets of ketone being swept out of the condenser with steam. Plugs of glass wool in the neck of the flask are used to prevent spray from being carried over.

Fifteen grams of sodium nitrate is dissolved in the distillate by shaking, for its salting-out effect. The toluene layer is then separated and the salt solution and containers are washed with two 5-ml. portions of benzene to rinse out all ketone. The accumulated solution containing the *p*-methylacetophenone is treated with 20 ml. of an approximately 0.5 *N* neutral solution of hydroxylamine hydrochloride in methanol, and allowed to stand overnight. The liberated hydrochloric acid is then titrated with a standard solution of sodium methoxide in methanol, using

(15) Used for all catalysts except antimony pentachloride, which was tested by use of the Perrier procedure [*Ber.*, **33**, 815 (1900)].

butter yellow as indicator. The titration is renewed at any convenient intervals, usually about twenty-four hours, until a permanent end-point is reached. This stepwise titration should be accompanied by a blank, and indeed the whole process of isolating and determining the ketone should be tested with known amounts. By such a test we can recover 99% of samples of acetophenone or *p*-methylacetophenone. Blanks may also be run through the whole procedure, omitting only the acetyl chloride, when there is any suspicion that a catalyst is somehow producing spurious evidence of yield, perhaps by catalytic decomposition of hydroxylamine.

Summary

1. Thirty-nine anhydrous metallic chlorides have been tested as catalysts for the Friedel-Crafts synthesis of *p*-methylacetophenone from acetyl chloride and toluene. Of these, twenty-eight showed no catalytic power at the boiling point of toluene. A comparison of most of the others, at optimum concentration and reaction time for each, yields the following order of decreasing efficiency: AlCl₃, SbCl₅, FeCl₃, TeCl₂, SnCl₄, TiCl₄, TeCl₄, BiCl₃, ZnCl₂. Of these, bismuth trichloride and tellurium dichloride have not previously been reported as catalysts.

2. Several of the catalysts produce a rapid decrease in yield as the reaction time is increased, doubtless because they catalyze auto-condensation of the product.

3. Several of the catalysts, notably titanium tetrachloride, give maximum yields at catalyst/acid chloride ratios several times greater than the 1:1 value often recommended.

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Dielectric and Solvent Effects upon the Iodide-Persulfate Reaction

BY EDWARD S. AMIS AND JAMES E. POTTS, JR.

Amis and co-workers¹⁻³ have begun an extensive investigation of ion-ion and ion-dipole reactions in various mixed solvents of controlled dielectric constant, in order to inquire into the electrostatic effects of the solvent and also the specific solvent effects upon a given reaction.

The alteration of the coulombic energy of activation for a reaction with a change in the dielectric constant of the solvent may be calculated from the equation¹

$$\Delta E_c^* = \frac{-Z_1 Z_2 e^2}{D_1 D_2 r} \Delta D \quad (1)$$

Also, the differences in energies of activation for a reaction when measured in media of constant composition and isodielectric media may be calculated by the equation derived by Amis and Holmes.³ This equation may be written

$$\Delta E_c^{*'} - \Delta E_D^{*'} = \frac{Z_1 Z_2 e^2 N T}{D^2 J} \left(\frac{1}{r} - \frac{3e}{10} \sqrt{\frac{2\pi N \mu}{10 D k T}} \right) \frac{dD}{dT} \quad (2)$$

By combining these equations the authors have obtained the expression

(1) E. S. Amis, *THIS JOURNAL*, **63**, 1606 (1941).
 (2) E. S. Amis and S. E. Cook, *ibid.*, **63**, 2621 (1941).
 (3) E. S. Amis and F. C. Holmes, *ibid.*, **63**, 2231 (1941).