

droxylamine hydrochloride method as before. In these cases, the catalyst was caused to react with the acid chloride previous to the addition of the aromatic compound.

The curves in Fig. 1, compared to those of the earlier work in which the catalyst was added to a mixture of the acid chloride and aromatic compound, indicate that performing the reaction under these conditions improves the yield given by catalysts previously found good, but lowers that produced by those previously found poor or only mediocre. Titanium tetrachloride is the lone and conspicuous exception to this generalization. Additional experiments have shown that the Perrier procedure followed by heating at 80–110° produces yields better than those reported in the previous paper, but not so good as those represented in Fig. 1.

The tests of antimony pentachloride at two concentrations were undertaken to learn whether an increased amount of catalyst would have the same effect as prolonged reaction time. It will be seen that the maximum yield is the same for both cases, but is produced more rapidly by more catalyst.

This is the first report of columbium pentachloride as a catalyst for the ketone synthesis, although it has been tested for alkylation.⁴ It is evidently equal to aluminum chloride in maximum yield produced but not in speed. The unexpected earlier finding that tellurium dichloride is a better catalyst than tellurium tetrachloride at temperatures of the steam-bath is not duplicated here. The single trial with beryllium chloride was not performed at the optimum conditions under which Brederick, Lehman, Fritzsche and Schonfeld⁵ secured a yield of 80%. Selenium tetrachloride is to be added to the list of chlorides having no catalytic effect upon this reaction.

Schroeder and Brewster⁶ have reported mercuric chloride to catalyze the Friedel-Crafts reaction of benzoyl chloride with diphenyl ether, whereas earlier work in this Laboratory² showed that this halide would not cause the formation of *p*-methylacetophenone. To test the indispensability of mercuric chloride in the former reaction, a run was made following the procedure of Schroeder and Brewster in all particulars except that no catalyst was added. The resulting mix-

ture, evaporated to about 1 ml. under reduced pressure, liberated hydrochloric acid from hydroxylamine hydrochloride and gave a solid derivative with phenylhydrazine. It cannot be said that mercuric chloride is not a catalyst, however, since the yield without it was far inferior to that obtained by Schroeder and Brewster.

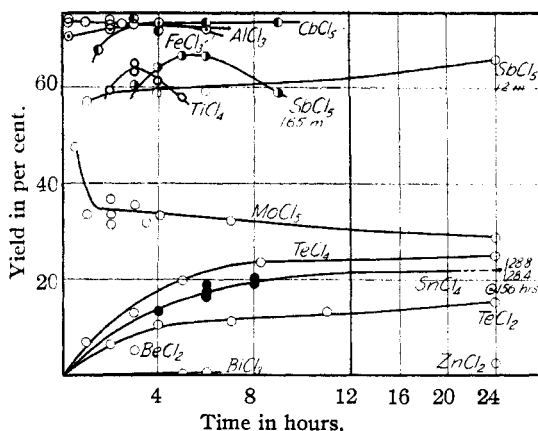


Fig. 1.—Relation between reaction time and yield. Ratios of catalyst/acid chloride were as follows: AlCl_3 , 1.6; CbCl_5 , 1.3; FeCl_3 , 1.2; SbCl_5 (a), 1.65; SbCl_5 (b), 1.2; TiCl_4 , 3.0; MoCl_5 , 1.2; TeCl_4 , 1.0; SnCl_4 , 2.0; TeCl_2 , 1.8; BeCl_2 , 1.2; ZnCl_2 , 0.8; BiCl_3 , 1.0.

Experimental

Most of the reagents were those described in the previous article. Columbium pentachloride and selenium tetrachloride were prepared by chlorinating the element at elevated temperatures, but the beryllium chloride was purchased.

Only two significant deviations from the original procedure were adopted. When the Perrier order of combining reagents is used, initial cooling in ice water is necessary to prevent loss of acetyl chloride, since there is usually an exothermic reaction producing a molecular compound of the catalyst and the acid chloride. The dripping of toluene down through a scrubber plug in the reflux condenser proved unnecessary, since the addition compound binds acid chloride and since reactions were in general less vigorous at the lower temperatures.

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STILLWATER, OKLAHOMA RECEIVED NOVEMBER 6, 1941

The Rate Equations for Consecutive Reactions

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The purpose of the present note is to point out explicitly the way in which several well-known procedures in differential equations may be of use in providing a completely general method of attack in solving the system of first order dif-

(4) Grosse and Ipatieff, *J. Org. Chem.*, **1**, 559 (1937).

(5) Brederick, Lehman, Fritzsche and Schonfeld, *Ber.*, **72**, 1414 (1939); *Angew. Chem.*, **52**, 445 (1939).

(6) Schroeder and Brewster, *THIS JOURNAL*, **60**, 752 (1938).

ferential equations corresponding to a set of consecutive or chain reactions.

First Order Reactions.—If all the reactions of the series are first order, the equations are linear in the dependent variables (concentrations) and may be solved by the method of Rakowski¹ or by differentiating them a number of times sufficient to make possible the attainment, by elimination, of a higher order differential equation in a single dependent variable. This equation and the subsequent ones which must be solved are linear with constant coefficients and hence their solutions present no difficulty. The elimination in every case may be effected in a straightforward manner by setting equal to zero the determinant of the coefficients of those dependent variables to be eliminated and of their derivatives.

Higher Order Reactions.—A determinantal equation cannot be set up here, so the elimination must be made by a less direct procedure. Except in the simplest of cases the higher order differential equation so obtained can be solved only by resorting to an approximation procedure.

Suppose we have

$$\frac{dx_i}{dt} = f_i(x_1, \dots, x_n) \quad (i = 1, \dots, n) \quad (1)$$

$$\frac{d^m x_k}{dt^m} = f \left(x_k, \frac{dx_k}{dt}, \dots, \frac{d^{m-1} x_k}{dt^{m-1}} \right) \quad (m \leq n) \quad (2)$$

and

$$x_i(0) = c_i, \quad (i = 1, \dots, n) \quad (3)$$

where c_i is the initial concentration and x_i the concentration at the time t of the i -th of the n reacting substances, and where (2) results from (1) by elimination. The functions f_i are of the general form

$$f_i(x_1, \dots, x_n) = \sum_j \beta_j \left(\frac{\pi x_i}{k_j} \frac{a_k b_j}{k_j} \right)$$

It will usually prove more convenient, if an approximation is necessary, to employ (1) directly, using (3) as initial guesses. Applying the method of successive approximations, we have

$$x_{i1} = \int_0^t f_i(c_1, \dots, c_n) dt + c_i \quad (i = 1, \dots, n)$$

as first approximations, and as $(j+1)$ -th approximations

$$x_{i,j+1} = \int_0^t f_i(x_{1j}, \dots, x_{nj}) dt + c_i \\ (j = 1, \dots, n; \quad j = 1, 2, \dots)$$

thus leading to solutions of any desired degree of accuracy.

(1) A. Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

Alternatively, we may apply the same method to

$$\frac{dx_k}{dt} = u_1, \frac{du_1}{dt} = u_2, \dots, \frac{du_{m-1}}{dt} = f(x_k, u_1, \dots, u_{m-1})$$

using as initial guesses

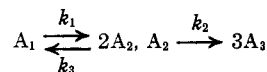
$$x_k = c_k, u_1 = f_k(c_1, \dots, c_n)$$

and

$$u_{i+1} = \left[\frac{d^i}{dt^i} f_k(x_1, \dots, x_n) \right]_{t=0} \quad (i = 1, \dots, m-2) \\ = [u_{i+1}(x_1, \dots, x_n)]_{x_1=c_1, \dots, x_n=c_n} \\ (i = 1, \dots, m-2) \quad (4)$$

where use has been made of (1) and derivatives of (1) in writing (4). This, then, gives the approximation $x_k = x_k(t)$. The remaining x 's may be arrived at in an analogous manner, or, when possible, by substitutions in (1)

As an example we may take



which might represent the biologically important system: glucose \rightleftharpoons lactic acid \rightarrow carbon dioxide. We have, corresponding to (1)

$$\left. \begin{aligned} \frac{dx_1}{dt} &= k_3 x_2^2 - \frac{1}{2} k_1 x_1 \\ \frac{dx_2}{dt} &= k_1 x_1 - \frac{1}{3} k_2 x_2 - 2k_3 x_2^2 \\ \frac{dx_3}{dt} &= k_2 x_2 \end{aligned} \right\} \quad (5)$$

and

whence

$$\frac{d^2 x_2}{dt^2} + (a + b x_2) \frac{dx_2}{dt} + c x_2 = 0$$

where

$$a = \frac{1}{2} k_1 + \frac{1}{3} k_2, \quad b = 4k_3, \quad \text{and} \quad c = \frac{1}{6} k_1 k_2$$

Using the first method we obtain

$$x_{11} = c_1 + \left(k_3 c_2^2 - \frac{1}{2} k_1 c_1 \right) t \\ x_{21} = c_2 + \left(k_1 c_1 - \frac{1}{3} k_2 c_2 - 2k_3 c_2^2 \right) t$$

and

$$x_{31} = c_3 + k_2 c_2 t$$

as first approximations which we put in the right-hand members of (5), leading to a set of second approximations, etc.

The alternative method would employ here the equations

$$\frac{dx_2}{dt} = u_1 \quad \text{and} \quad \frac{du_1}{dt} = -(a + b x_2) u_1 - c x_2$$

with initial guesses

$$x_2 = c_2 \quad \text{and} \quad u_1 = k_1 c_1 - \frac{1}{3} k_2 c_2 - 2k_3 c_2^2$$

Then

$$x_{21} = c_2 + \left(k_1 c_1 - \frac{1}{3} k_2 c_2 - 2k_3 c_2^2 \right) t$$

and

$$u_{11} = [1 - (a + b c_2) t] \left(k_1 c_1 - \frac{1}{3} k_2 c_2 - 2k_3 c_2^2 \right) - c c_2 t,$$

etc.

This example was suggested by Mr. Manuel F. Morales of the Department of Physiology.

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RECEIVED MAY 16, 1941

The Influence of Electrolytes upon Ammonolysis by Liquid Ammonia

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Shatenshtein and Markova¹ have shown that the ammonolysis of pilocarpine by liquid ammonia is catalyzed markedly by certain salts and that the energy of activation for the catalyzed reactions is much greater than for reactions effected in the absence of catalysts. Similar results are obtained (Table I) when values for the energy of activation corresponding to the catalyzed ammonolysis of diethyl malonate and ethyl benzoate are calculated from data published by Audrieth and co-workers.^{2,3} These data together with those

TABLE I
AMMONOLYSIS OF ESTERS

	Conc. of NH ₄ Cl, M	Energy of activation, cal./mole
Diethyl malonate	None	3500
	0.15	8300
Ethyl benzoate	.37	8000
	.75	8300

of Shatenshtein and Markova show that, for the ammonolysis of ester-type linkages by liquid ammonia, both the rate of reaction and energy of activation are increased by the presence of an electrolyte or by an increase in the concentration of such an electrolyte. In view of these results, it seemed desirable to secure values for the energy of activation under similar conditions for the ammonolysis of 2-chlorobenzothiazole (a reaction involving a halide-type bond), the rate of which has recently been shown to be but little influenced by the presence of electrolytes.⁴

(1) Shatenshtein and Markova, *Acta Physicochim.* (U. S. S. R.), **11**, 131 (1939).

(2) Slobutsky, Audrieth and Campbell, *Proc. Nat. Acad. Sci.*, **23**, 611 (1937).

(3) Fellinger and Audrieth, *THIS JOURNAL*, **60**, 579 (1938).

(4) Lemons, Anderson and Watt, *ibid.*, **63**, 1953 (1941).

Experimental

Reagent grade ammonium carbonate, ammonium sulfamate prepared as described by Baumgarten⁵ and Audrieth,⁶ and ammonium carbamate prepared as described by Basaroff⁷ were used. Other materials and experimental methods were identical with those previously described.⁴

Results.—Data relating to the effect of certain salts upon the ammonolysis of 2-chlorobenzothiazole are summarized in Table II. Although in many cases the rate of reaction is increased slightly, the energy of activation is increased by all the electrolytes used. The results obtained using ammonium carbamate and ammonium carbonate constitute an exception to the recently published statement by Cheronis and Spitzmueller⁸ to the effect that the "carbamate effect" is "of general application in ammonolytic reactions."

TABLE II
AMMONOLYSIS OF 2-CHLOROBENZOTHIAZOLE

Electrolyte	k_{230} , hours ⁻¹	k_{310} , hours ⁻¹	Energy of activation, cal./mole
NH ₄ Cl (0.314 M)	0.0185	0.0432	15,000
NH ₄ O ₂ CC ₆ H ₅ (0.314 M)	.0175	.0431	15,900
NH ₄ SO ₃ NH ₂ (0.314 M)	.0176	.0412	15,000
NH ₄ CO ₂ NH ₂ (satd.)	.0163	.0395	15,700
(NH ₄) ₂ CO ₃ (satd.)	.0158	.0386	15,800
NaCl (0.314 M)	.0184	.0446	15,600
KCl (satd.) ^a	.0172	.0410	15,300
None	.0186	.0405	13,700

^a We wish to call attention to the fact that in Table III of an earlier paper,⁴ it should have been indicated that the potassium chloride solution used was *saturated*, and not 0.314 M.

Liquid ammonia is a solvent of comparatively low dielectric constant, and it would seem probable that salt effects in liquid ammonia solutions would be more pronounced than in aqueous solutions. Since in many cases concentration data, etc., are known only approximately, it is not possible to make quantitative calculations on interionic effects, etc., from data at present available. However, the differences in the energy of activation in the presence and in the absence of a catalyst are greater than the probable experimental errors. The rate measurements on the ammonolysis of diethyl malonate gave results which were reproducible only to within 10%, partly because of autocatalysis by the malonamide. The values

(5) Baumgarten, *Ber.*, **69**, 1929 (1939).

(6) Audrieth, *et al.*, *Chem. Rev.*, **26**, 49 (1940).

(7) Basaroff, *J. prakt. Chem.*, **I**, 283 (1870).

(8) Cheronis and Spitzmueller, *J. Org. Chem.*, **6**, 349 (1941).