addition of some active catechol oxidase. To test this possibility preparation No. L was inactivated both by heat and with acid, after which it was added to preparation No. 70 and the activities again measured. In neither instance was there any indication of a non-enzymatic factor which operated with the catechol oxidase in bringing about the oxidation of *p*-cresol.

If there is a "factor" which together with catecholase catalyzes the aerobic oxidation of monohydric phenols, such as *p*-cresol, it is not nonenzymatic, since it has so many properties common to enzymes. Thus it is adsorbable to alumina and kaolin, completely precipitated by ammonium sulfate, does not pass through semipermeable membranes, is heat labile, readily inactivated by acid, and by methods generally employed in the purification of enzymes it has been possible to separate it partially from catechol oxidase.

It should be mentioned that so far the adsorption to alumina and kaolin has failed to affect the ratio of catechol oxidase to the activity responsible for the oxidation of *p*-cresol in the case of tyrosinase preparations obtained from the wild mushrooms, *Lactarius piperatus* and the common pasture puff ball, *Calvatia cyathiformis*. Both of these preparations were rich in activity toward *p*-cresol and poor in catechol oxidase.

Summary

1. The ratio of the activities toward catechol and *p*-cresol in tyrosinase preparations from the common mushroom, *Psalliota campestris*, can be varied by adsorption of the enzymes to alumina and kaolin.

2. By means of partial adsorption it is possible to obtain preparations in the residual solution rich in catechol oxidase and poor in activity toward *p*-cresol.

3. The ratio of the activity toward *p*-cresol to that toward catechol was greater in the elutate from the adsorption than in the original solution.

4. The activity toward *p*-cresol possesses properties common to enzymes in general. It is heat labile, inactivated by dilute acids, does not pass through semi-permeable membranes, and can be precipitated from solution by ammonium sulfate.

5. The catechol activity and the activity toward *p*-cresol are mutually independent.

6. So far attempts to affect the ratio of the catechol and *p*-cresol activities of tyrosinase preparations from the mushroom, *Lactarius piperatus* and the puff ball, *Calvatia cyathiformis*, have been unsuccessful.

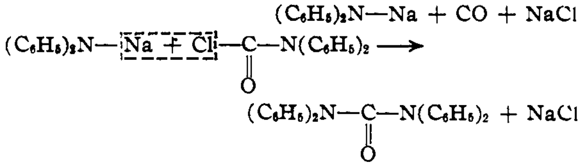
NEW YORK, N. Y. RECEIVED JUNE 25, 1938

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Reactions of Sodium and Potassium on Acid Chlorides

BY IRWIN A. PEARL, THEODORE W. EVANS AND WILLIAM M. DEHN

In a prior article[1] it was reported that diphenylcarbamine chloride treated with sodium in boiling toluene yielded tetraphenyloxamide. Further work now has shown conclusively that the reaction follows the more interesting course to form tetraphenylurea and carbon monoxide.[2] That tetraphenyloxamide was not first formed in the reaction was proved by the following experiments. Tetraphenyloxamide, prepared from diphenylamine and oxalyl chloride by the method of Stolle,[3] was treated with atomized sodium in boiling toluene under the same conditions as was the diphenylcarbamine chloride. No tetraphenylurea could thus be found, or from tetraphenyloxamide by heating for two hours at 195°. The reaction can be explained in the following manner



$$(C_6H_5)_2NC\begin{matrix}{}^{\nearrow O}\\ {}_{\searrow Cl}\end{matrix} + 2Na \longrightarrow (C_6H_5)_2N{-}\underset{\underset{Na}{|}}{C}\begin{matrix}{}^{\nearrow ONa}\\ {}_{\searrow Cl}\end{matrix} \longrightarrow$$

$$(C_6H_5)_2N{-}Na + CO + NaCl$$

$$(C_6H_5)_2N{-}\boxed{Na + Cl}{-}\underset{\underset{O}{\|}}{C}{-}N(C_6H_5)_2 \longrightarrow$$

$$(C_6H_5)_2N{-}\underset{\underset{O}{\|}}{C}{-}N(C_6H_5)_2 + NaCl$$

Proof of this type of mechanism was obtained by treating diphenylcarbamine chloride with an excess of sodium in toluene and obtaining sodium diphenylamine in the residue. These observa-

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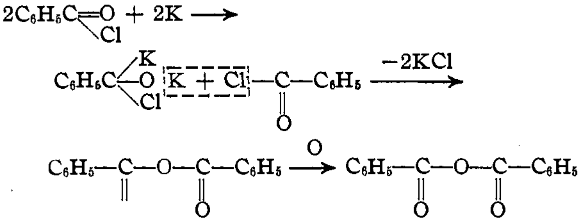
[1] Evans and Dehn, THIS JOURNAL, **52**, 3645 (1930).

[2] Hammerich [*Ber.*, **25**, 1826 (1892)] reported the reaction of ditolylcarbamine chloride with sodium in ether to give the oxamide derivative.

[3] Stolle, *ibid.*, **46**, 3916 (1913).

tions led to a study of the reaction of sodium and potassium on other acid chlorides.

Sodium reacts with benzoyl chloride in anhydrous ether solution to give ethyl benzoate as the main product. This reaction, with other metals, was reported by Varvoglis.[4] However, sodium or potassium reacts with benzoyl chloride in dry xylene to give benzoic anhydride and sodium chloride. This unique reaction, in which oxygen is obtained from the atmosphere, can be explained in the following simple manner



$$2C_6H_5C\overset{}{\lessgtr}^{O}_{Cl} + 2K \longrightarrow$$

$$C_6H_5C\overset{K}{\underset{Cl}{\lessgtr}}O\ \boxed{K + Cl}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \xrightarrow{-2KCl}$$

$$C_6H_5{-}\underset{\|}{C}{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \xrightarrow{O} C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5$$

In like manner phthalyl chloride and succinyl chloride react with potassium or sodium in dry xylene to give phthalic anhydride and succinic anhydride in 70 and 60% yields, respectively. *p*-Toluenesulfonyl chloride reacts with potassium to give di-*p*-tolyldisulfone and potassium chloride according to the following

$$2CH_3{-}C_6H_4{-}SO_2Cl + 2K \longrightarrow$$
$$CH_3{-}C_6H_4{-}SO_2{-}SO_2{-}C_6H_4{-}CH_3 + 2KCl$$

Experimental

Preparation of Tetraphenylurea.—To a mixture of atomized sodium in toluene was added one mole of diphenylcarbamine chloride and this mixture was boiled for a short time. The precipitated sodium chloride was filtered off and large, jewel-like crystals, in 66% yield, separated from the cooled filtrate. Recrystallization from toluene gave crystals melting at 182–183°. A mixed melting point with pure tetraphenylurea, prepared by the method of Michler and Zimmermann,[5] showed no depression. The gas evolved during the reaction was collected and analyzed. It proved to be carbon monoxide. Further proof that this compound is the urea and not the oxamide was obtained by the analytical data. In the prior paper there was given only the nitrogen value, which agreed equally well with either compound.

Calcd. % for	$(C_6H_5NCO)_2$	$(C_6H_5N)_2CO$	Found
C	79.6	82.4	82.3
H	5.1	5.5	5.9
N	7.1	7.7	7.5
O	8.2	4.4	4.3 diff.

Reaction of Diphenylcarbamine Chloride with Excess of Sodium.—Diphenylcarbamine chloride was added to an excess of atomized sodium in boiling toluene for thirty minutes. The mixture was filtered and well washed with toluene. The filtrate and washings were evaporated to a small volume and, upon cooling, yielded crystals of tetraphenylurea melting at 182–183°. Part of the sandy precipitate from the original filtration was treated with water. Diphenylamine melting at 50–52° separated. The rest of this sandy precipitate was treated with benzoyl chloride and, after warming, washed well with dilute sodium carbonate solution; recrystallizing from alcohol yielded crystals of benzoyldiphenylamine melting at 176–177°. When potassium was substituted for sodium in this experiment, the same results were obtained.

Reaction of Benzoyl Chloride and Sodium in Anhydrous Ether.—A mixture of 1.1 g. of atomized sodium in 50 cc. of dry xylene was decanted and after washing with absolute ether the sodium was covered with 50 cc. of absolute ether. To this mixture was added 7 g. of benzoyl chloride. The flask was stoppered and allowed to stand for ten days with occasional shaking. The contents were then filtered and the ethereal filtrate was evaporated. A residue of 6.5 g. of ethyl benzoate boiling at 210–213° was obtained.

That ethyl benzoate was not formed by the reaction of benzoyl chloride with absolute ether was proved by a mixture of the two without sodium. The benzoyl chloride was recovered quantitatively with no trace of ethyl benzoate.

Reaction of Benzoyl Chloride and Potassium in Anhydrous Xylene.—Two grams of potassium was atomized in 50 cc. of dry xylene and allowed to cool. To this was added 7 g. of benzoyl chloride and the mixture was heated occasionally for two days. After disappearance of all the potassium, the potassium chloride was filtered off and the xylene filtrate was evaporated on the steam-plate. A heavy oil was obtained and, on standing, this yielded light colored crystals. After drying on a porous plate and recrystallizing from ether, they melted at 41–42°. A mixed melting point with pure benzoic anhydride showed no depression.

Reaction of Phthalyl Chloride and of Succinyl Chloride with Potassium and Sodium.—A mixture of 10.1 g. of phthalyl chloride and 4.0 g. of atomized potassium in 100 cc. of xylene was heated to boiling and allowed to stand for three weeks. The potassium chloride was filtered off and the filtrate yielded 5.3 g. (70%) of phthalic anhydride. Recrystallization from benzene gave white needles melting at 130–131°. A mixture with pure phthalic anhydride melted at the same temperature.

Six grams of succinyl chloride and 2 g. of sodium were treated in the same manner for eight weeks. A yield of 2.5 g. (60%) of succinic anhydride melting at 116–118° was obtained. Recrystallization from absolute alcohol yielded crystals melting at 118–119°. A mixture with pure succinic anhydride melted at the same temperature.

Reaction of *p*-Toluenesulfonyl Chloride with Potassium or Sodium.—To a mixture of 4 g. of atomized potassium and 100 cc. of warm xylene was added gradually 19 g. of *p*-toluenesulfonyl chloride. The vigorous reaction taking place after each addition was allowed to subside before the next addition. After all the chloride was added the

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[4] Varvoglis, *Ber.*, **70**, 2391 (1937). This author treated acid chlorides in absolute ether with a large number of metals. Of all the metals tried, only iron and zinc were effective, and these yielded ethyl esters of the respective acids On the basis of this work, potassium and sodium probably would have been predicted to be without action.

[5] Michler and Zimmermann, *ibid.*, **12**, 1166 (1879). These authors prepared the urea by treating diphenylcarbamine chloride with diphenylamine.

mixture was allowed to cool. All the potassium had disappeared and the reaction mixture was thick with precipitate. The mixture was filtered and the precipitate was dried. The precipitate was treated with water and extracted with ether. The ethereal extraction upon evaporation yielded 3 g. of crude di-*p*-tolyldisulfone melting at 214–218°. Recrystallization from benzene yielded crystals melting at 220–221°.

Summary

1. Diphenylcarbamine chloride and sodium or potassium yield tetraphenylurea and carbon monoxide with the intermediate formation of sodium or potassium diphenylamine.
2. Benzoyl chloride and sodium or potassium in anhydrous ether yield ethyl benzoate.
3. Acyl chlorides with sodium or potassium in xylene yield acid anhydrides.
4. *p*-Toluenesulfonyl chloride yields di-*p*-tolyldisulfone when treated with sodium or potassium in xylene.

SEATTLE, WASHINGTON RECEIVED JULY 11, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. PETER'S COLLEGE]

The Catalytic Properties of Charcoal. II. Further Studies on the Indophenol Reaction

BY JAMES F. O'BRIEN, VINCENT TKAC AND CLAUDE SCHWOB

The unusual factors encountered in a previous study of the activity of charcoal in catalyzing the hydrogen peroxide oxidation of a mixture of α-naphthol and *p*-phenylenediamine at *p*H 4.5 to form indophenol[1] prompted us to continue our studies of this interesting reaction.

Two aspects of this oxidation particularly suggest further investigation. What is the cause of the decrease in yield of the indophenol after one-half minute? What is the role of the charcoal in these oxidative reactions? In the present paper we attempt to give a partial answer to the first question. The third paper of this series will treat of certain findings relative to the second question.

We first repeated the original work[1] under carefully controlled conditions, using a so-called "pure" sucrose charcoal. At both 30 and 40° we confirmed our former findings, the yield being at a maximum at one-half minute and then decreasing to a value which remained constant after seven minutes. As before, the indophenol was found to be strongly adsorbed by the charcoal so that the latter and the filtrate were analyzed separately. Figure 1 shows the amount of indophenol present at various times. The charcoal furnished the bulk of the indophenol (curve 1), but a definite peak at one-half minute shows in the filtrate curve (curve 2).

The ratio of the total yields of the reaction at 40° to those of the reaction at 30° at corresponding times gives us a series of numbers which are akin to temperature coefficients (Table I). It will be noticed that these ratios increase linearly with time until, after two minutes, they approach a constant value. A rough calculation of the apparent energies of activation for these reaction times was made by substituting these coefficients in the Arrhenius equation. It is to be emphasized that Hinshelwood[2] and others have pointed out that such a substitution cannot give the true energy of activation for a heterogeneous reaction. It is interesting to note, however, that the values obtained for E as well as for the temperature coefficients show that two distinct processes are going on in this reaction, one predominating in the first two minutes, the second one after that. The energy of activation was likewise determined for the uncatalyzed formation of indophenol at 30 and 40° (Fig. 1, curves 5 and 6), and found to be approximately 5000 cal.

TABLE I

Time, min.	Temp. coeff.	E, cal.
0.25	1.083	1400
.5	1.138	2300
1	1.198	3300
2	1.238	3900
4	1.239	3900
7	1.239	3900
14	1.241	3900
28	1.245	4000

The progressive increase in the value of E for the catalyzed reaction suggests either of two possibilities: the charcoal suffers poisoning as the

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[1] Paper I. Schwob, THIS JOURNAL, **58**, 1115 (1936).

[2] Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," The Clarendon Press, Oxford, 1933, p. 348, *et seq.*