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The Reactivity of Atoms and Groups in Organic Compounds. XVI. The Relative Effects of Substituents on the Rates at which Certain Acyl and Alkyl Chlorides React with Ethyl Alcohol[1]

BY JAMES F. NORRIS, E. V. FASCE AND CYRIL J. STAUD

In the use of rates of reactions to study the effect of structure on the relative reactivities of a particular bond in a series of similar compounds it seemed of interest to investigate the reactions of benzoyl chloride and certain of its substitution products with ethyl alcohol. The rates have been determined at which a number of substituted benzoyl chlorides, $XC_6H_4CH_2Cl$, react with a mixture of water and acetone.[2] The substituted benzoyl chlorides differ from substituted benzyl chlorides in that the former have oxygen instead of hydrogen linked to the carbon atom in combination with chlorine. The determination of the relative rates at which the members of the two series react with a fixed reagent would show the effect of the replacement of hydrogen by oxygen and the relative activating influence of each substituent in the ring in the two classes of compounds. The mechanism of the reactions involved in the two series must be understood before a satisfactory interpretation of the results is reached.

Three simple hypotheses in regard to the mechanisms of the reactions in the two classes may be mentioned. First, the mechanism is the same with both acyl and alkyl chlorides. In this case the reactions involve the direct replacement of chlorine by ethoxyl and the liberation of hydrogen chloride. The results under these conditions would show the activating influence of substituents in the ring on the carbon–chlorine bonds of both the acyl and the alkyl chlorides. Second, the mechanisms of the reactions in the two series are different. In the substituted alkyl chlorides the replacement is as postulated above and the substituents affect the lability of the carbon–chlorine bond. In the acyl chlorides the alcohol adds to the carbonyl group and forms an unstable product which decomposes into the ester and hydrogen chloride. In this case the rates at which addition and decomposition take place determine the observed rate of the reaction. If addition is the slower of the two reactions involved, it is this that is measured. The observed rates are accordingly a measure of the relative reactivities of the carbonyl bond as affected by the substituents in the ring. Third, the acyl chloride forms an oxonium salt by adding to the oxygen atom of the alcohol and this product then decomposes into the ester and hydrogen chloride.

In this paper the experimental results are given and certain conclusions drawn from these results irrespective of theory. Experiments of a different type are necessary in order to elucidate the mechanism of the reactions involved. Such experiments are now in progress because a correct interpretation of reactivity as deduced from velocity constants can be reached only after the mechanism of the reactions involved is understood.

If the relative rates at which the derivatives of benzyl chloride react with a mixture of alcohol and water are compared with those with which benzoyl chlorides react with alcohol it is seen that the replacement of two hydrogen atoms in the benzyl chlorides by an oxygen atom led to the result that substitution in the ring of the acyl chlorides had the opposite effect from that produced by similar substitution in the benzyl chlorides.

Since the conditions under which the velocity constants were determined in the two series of compounds were not the same, more definite comparisons can be made between the acyl chlorides and the derivatives of diphenylchloromethane, which may be considered as derived from benzyl chloride by the replacement of one hydrogen atom by a phenyl radical. These compounds have been studied in this Laboratory[3,4,5] under the same conditions used with the acyl chlorides, namely, in solutions in alcohol at 0°. The extent to which reaction took place was determined in both cases by measuring the changing electrical

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[1] From the theses presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy by Cyril J. Staud, 1924, and E. V. Fasce, 1932.

[2] Olivier, *Rec. trav. chim.*, **49**, 996 (1930).

[3] Norris and Morton, THIS JOURNAL, **50**, 1795 (1928).

[4] Norris and Banta, *ibid.*, **50**, 1804 (1928).

[5] Norris and Blake, *ibid.*, **50**, 1808 (1928).

conductivity of the solutions as the reaction proceeded. The order of the influence of the substituent was, in general, the same as in the case of the substituted benzyl chlorides.

In Table I are given the relative velocity constants of the reaction between ethyl alcohol and certain substituted benzyl chlorides; some of the numbers are taken from the work of Norris and H. H. Young, Jr.[6] For comparison are given the results of other significant investigations.

TABLE I

RELATIVE VELOCITY CONSTANTS

First Order. Type Compound = 1

I. $XC_6H_4COCl + C_2H_5OH$. Temp. 0°. K_0/min. $C_6H_5COCl = 0.0044$

II. $XC_6H_4COCl + (CH_3)_2CHOH$. Temp. 25°. K_{25}/min. $C_6H_5COCl = 0.00385$[7]

III. $XC_6H_4COCl + H_2O$ in $(CH_3)_2CO$. Temp. 0°. K_0/min. $C_6H_5COCl = 0.026$[8]

IV. $XC_6H_4C_6H_5CHCl + C_2H_5OH$. Temp. 25°. K_{25}/min. $(C_6H_5)_2CHCl = 0.00290$[3,4,5]

V. $XC_6H_4CH_2Cl + H_2O$ in $(CH_2)_2CO$. Temp. 60°. K_{60}/min. $C_6H_5CH_2Cl = 0.00046$[2]

Substituent	I $RCOCl +$ C_2H_5OH	II $RCOCl +$ $(CH_3)_2CHOH$	III $RCOCl +$ H_2O	IV $XC_6H_4C_6H_5CHCl +$ C_2H_5OH	V $XC_6H_4CH_2Cl +$ $H_2O(CH_3)_2CO$
o-CH_3	3.7	...	...	2.9	4.1
m-CH_3	0.85	...	1.5	2.1	1.2
p-CH_3	.78	0.64	2.9	16.2	8.7
o-CH_3O	29	...	...	93	...
m-CH_3O	1.1	...	...	...	...
p-CH_3O	0.81	...	...	1200	...
o-Cl	3.5	...	1.5	0.01	0.30
m-Cl	5.6	...	1.5	.045	.20
p-Cl	1.9	1.5	0.85	.42	.58
o-Br	3.4	...	1.4	...	.28
m-Br	4.6	...	1.7	...	.20
p-Br	2.1	1.8	0.9	.33	.51
o-I	2.9	...	...	...	.27
m-I	4.1	...	...	...	.19
p-I	1.9	1.3	...	...	.47
o-NO_2	2.2	1.9	1.8	...	.10
m-NO_2	20.5	...	6.9	...	...
p-NO_2	21.6	10.5	11.5	...	.10

The following facts can be drawn from the table.

(1) From I and II. The effects of substituents on the relative rates in the ethyl alcohol series at 0° are greater than those in the isopropyl alcohol series at 25°. The activating effects of the several groups fall in the same order in the two series.

(2) From I and III. At 0° benzoyl chloride reacts six times as rapidly with water (mixed with acetone) as with ethyl alcohol. With the exception of methyl the effect of the introduction of substituents is greater in the reaction with alcohol. The relative effects of the position of a given substituent are the same in the two series except in the case of methyl.

(3) From I and V. The introduction of halogen atoms and the nitro group increases the reactivity of the acyl chlorides and decreases the reactivity of the substituted alkyl chlorides. The methyl radical in the meta and para positions decreases reactivity in the acyl chlorides and increases reactivity in the alkyl chlorides. The methyl radical in the ortho position increases reactivity in both series and is the only exception to the reversal effect brought about by replacement of two hydrogen atoms in the benzyl compounds by an oxygen atom.

(4) From I and IV. The difference between substituted acyl and alkyl halides is brought out more strikingly in these series in which the velocity constants were determined under the same conditions, namely, at 0° and as first order reactions with ethyl alcohol. The effect of substituents on the reactivity of the C—Cl bond in the derivatives of diphenylchloromethane is very great and the differences are as a result also great. A chlorine atom in the ortho position increases the rate of reaction of the acyl chloride 3.5 times and reduces the rate of the alkyl chloride to 0.01. The methyl radical in the para position decreases the rate of the acyl chloride to 0.78 and increases the rate of the alkyl chloride to 16.2. These

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(6) Norris and H. H. Young, Jr., THIS JOURNAL, **57**, 1420 (1935).

(7) Norris and Gregory, *ibid.*, **50**, 1813 (1928).

(8) Berger and Olivier, *Rev. trav. chim.*, **46**, 516 (1927).

differences are even more marked in the methoxyl derivatives. The effects on reactivity in all cases are reversed in the two series except in the case of *o*-methyl.

(5) A close examination of I yields the following conclusions.

The substituents studied differ widely in their effects. At one extreme is the methoxyl group, which greatly increases reactivity when in the ortho position and decreases reactivity slightly in the para position; in the meta position the effect is close to that of the para position. Methyl resembles methoxyl. At the other extreme is the nitro group, which greatly increases reactivity in the para position, and only slightly in the ortho position; the effect in the meta position is close to that in the para. All the halogens stand in an intermediate position. The greatest effect is in the meta position; there is not such a great difference in the three positions. The activating influence decreases from chlorine to bromine to iodine.

The order of the activating effects of the several substituents in different positions is shown below:

In ortho compounds: NO_2(2.2), I(2.9), Br(3.4), Cl (3.5), CH_3(3.7), CH_3O(29).

In meta compounds: CH_3(0.85), CH_3O(1.1), I(4.1), Br(4.6), Cl(5.6), NO_2(20.5).

In para compounds: CH_3(0.78), CH_3O(0.81), Cl(1.9), I(1.9), Br(2.1), NO_2(21.6).

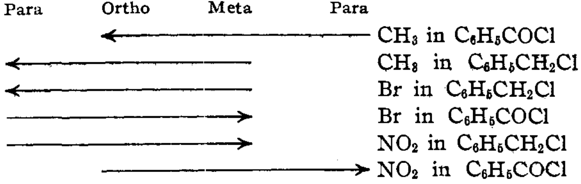
The effect of position on the activating influence of a substituent is shown to be very great in the case of the nitro and methoxyl groups.

The change in activating effect with the nature of the group and its position in the acyl and alkyl series is shown in Table II.

TABLE II

EFFECT OF THE POSITION OF SUBSTITUENTS ON REACTIVITY

The direction of the arrow indicates increasing reactivity.



It is seen from Table II that bromine is intermediate in its effect between methyl and the nitro group and that in the two series of halogen compounds the effects are opposite. The methyl radical has an opposite effect from that of the nitro group in both the acyl and alkyl derivatives.

It has been shown in this paper that the relative values of the activating influence of substituents are dependent upon the nature of compound into which the substituent is introduced, the nature of the substance with which the bond reacts and the nature of the substituent and its position.

The temperature coefficients of the reactions involved in making comparisons are of great importance. If these vary but slightly comparisons made at different temperatures lead to similar results. It is possible, however, to bring about changed relationships in reactivity at different temperatures when the several reactions are differently accelerated by heat. This phase of the subject is considered in the paper by Norris and Young.[6]

The results given in this paper will be of value in interpreting the facts with the use of the theory of the electronic structure of molecules after more data which are necessary have been determined.

Experimental Details

Apparatus.—The form of the apparatus used to measure the conductivity of the solutions of the acyl chlorides was essentially that described by Hall and Adams.[9] A Kohlrausch slide wire bridge with extension coils (Leeds and Northrup No. 4258) and two variable resistance boxes (Leeds and Northrup No. 47115 and 4656) with a range of 1000–110,000 ohms were used. The bridge was energized by a 1000 cycle audio oscillator, the vibrator of which was a tuning fork operated by four dry cells. Between the bridge and the receiver were inserted two stages of audio frequency amplification employing three element thermionic valves. The amplification ratio was approximately 10:1. All wire connections were soldered and the entire apparatus was grounded. The bridge was calibrated twice.

A Washburn Type B conductivity cell was used. The cell constant was determined by making a series of readings with the slide wire at different positions on the bridge, calculating the corresponding cell constant in each case and averaging the results. The thermostats held the temperature constant to ±0.05°.

Preparation of Materials.—It was necessary to obtain alcohol as free from water as possible because the presence of even a small percentage of the latter affects the conductivity of hydrogen chloride in the solvent. The ethyl alcohol used by Fasce was refluxed several times with lime and distilled. The first part of the distillate was rejected in each case. The final refluxing and distillation was carried out in a stream of dry nitrogen free from oxygen. Three samples obtained in this way, which boiled at a constant temperature, were combined, refluxed again over lime and distilled in nitrogen. The first portion which came over under high reflux ratio was discarded, and the main fraction collected in a dry reservoir filled with nitrogen. The reservoir was a glass bottle closed with an all

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[9] Hall and Adams, THIS JOURNAL, 41, 1515 (1919).

glass stopper so constructed that dry nitrogen free from oxygen could be forced into the bottle and cause the alcohol to flow out. A mercury seal prevented any access of air at the stopper. The density of the alcohol was determined at 25° when first prepared and after storage for one and three months. The values were, respectively, 0.78510, 0.78509 and 0.78512. The value given by the U. S. Bureau of Standards is 0.78505. The two samples used by Staud had the density 0.78504 and 0.78509.

The *acyl chlorides* were prepared from pure samples of the acids, except in the case of benzoyl chloride, which was obtained in pure condition as the result of fractionation of a C. P. sample. In the preliminary work the acids were treated with phosphorus pentachloride but later thionyl chloride was used. After the excess of the latter was removed the chlorides were distilled under diminished pressure through an efficient fractionating column and collected out of contact with air in capsules that were later sealed. In the case of the solid chlorides cooling curves were made as a final test of purity. The thermometers used were graduated in 0.1° and were calibrated.

Mechanism of the Reaction.—In the study of the rate at which diphenylchloromethane reacted with ethyl alcohol it was shown that the reaction was reversible,[9] and a new method of handling the data was devised to calculate the velocity constant of the reaction. It seemed desirable, therefore, to investigate the reaction with acyl chlorides from this point of view and to determine whether any side reactions took place. The reversibility was tested by Fasce in two experiments. In the first, 20 g. of pure ethyl *p*-nitrobenzoate was placed in an all-glass apparatus held at 80–86° and a slow current of dry hydrogen chloride was bubbled through the molten ester for four and one-half hours. The resulting material was then powdered and placed in a vacuum desiccator to remove the hydrogen chloride. Cooling curves of the material and of a sample of the pure ester were made and the melting points (56.00°) were found to be identical. A cooling curve of the pure ester mixed with 1% of *p*-nitrobenzoyl chloride gave no horizontal part with the highest point 0.70° below the true melting point.

In the second experiment the conditions more closely approached the conditions under which the conductivity measurements were made. Dry hydrogen chloride was passed for two hours at 25° through a solution containing 10% by weight of the ester in absolute ethyl alcohol. The latter was removed under diminished pressure and a cooling curve made of the resulting material after drying in a vacuum. No change in the ester had taken place.

It seemed possible that the acyl chloride might react with the alcohol and form ethyl chloride and the free acid, which in turn would be converted in the presence of hydrogen chloride into the ester and water. If such a side reaction took place to a very limited extent it would have a great effect on the result, because Goldschmidt[10] has shown that 0.15% of water in ethyl alcohol–hydrochloric acid solution lowers the specific conductance 17–20%. To test the possibility of the formation of ethyl chloride a 0.1 formal solution of *p*-nitrobenzoyl chloride in ethyl alcohol was allowed to react for two hours at 25°. The liquid was distilled off into a receiver cooled by solid carbon dioxide and ether, fractionated and the lower fraction vaporized and examined. No ethyl chloride was found. A control experiment in which ethyl chloride was introduced into the reagents showed that it could be separated and identified. The solid residue from the test was shown to contain no acid. The conclusions from these experiments that the reaction was irreversible and that the conductivity measurements gave a true index of the percentage conversion at any time were confirmed in the experiments in which the velocity constants were determined.

Experimental Procedure.—Extreme precautions were taken to introduce into the conductivity cell a solution made up of weighed quantities of absolute alcohol and the acid chloride with as little as possible air or moisture. In the work of Fasce all operations were carried out in containers filled with dry nitrogen. The liquid acyl chlorides were drawn up into a calibrated pipet and the desired volume, calculated from the density, introduced into a very thin glass weighed capsule, filled with nitrogen. The capsule was sealed and weighed and the exact weight of the chloride determined. The capsule was next placed in a vessel, with glass stopper, which contained the weighed alcohol that had been brought to the temperature of the thermostat. The capsule was broken and the solution mixed by violent shaking. The vessel was connected with the conducitivity cell, the solution drawn in by suction, and the stopcocks of the cell were closed. The times required for the several operations were noted. The initial measurements of conductivity were made within two to four minutes after the solution had been introduced into the cell. A total of twelve to fourteen readings were made at time intervals over the range of 5 to 90% conversion. The final observations were extended until no further change in resistance was apparent. With two observers it was possible to determine with accuracy the resistances during the early stages of reactions that were very rapid.

In certain cases the material in the cell and the unused portion of the solution in the reservoir were analyzed for hydrochloric acid by titration with *N*/30 sodium hydroxide. The results served as a check on the calculations of the formality of the solution from the weighed quantities used and from the final conductance after correcting for the effect on the conductance produced by the presence of the ester formed in the reaction. In the case of ethyl benzoate the lowering of the conductivity of several concentrations of hydrochloric acid in alcohol due to the presence of the ester was directly measured and found to be 3.5% for solutions 0.1 molal in ethyl benzoate.

Calculation of the Velocity Constants.—In the earlier calculations the conductance values of hydrogen chloride in alcohol at 0° determined by Lapworth and Partington[11] were used. It was found that the constants calculated from the first part of the reaction were always lower than the average and those after 50% conversion were higher. This result came either from faults in our measurements or the inaccuracy of the conductance table. A critical examination of the

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(10) Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914).

(11) Lapworth and Partington, *J. Chem. Soc.*, **99**, 1426 (1911); Partington, *ibid.*, **99**, 1939 (1911).

results of Lapworth and Partington at 25° with those of Goldschmidt at 25° brought out the fact that the former were lower than the latter, the difference varying from 3.6 to 13.5%. The results of Goldschmidt had been checked in this Laboratory by Norris and Morton.[3] It seemed probable from the work of Goldschmidt that the alcohol of Lapworth and Partington contained a trace of water. As little as 0.052% of water would account for the differences in conductivity found by the two observers. It seemed possible that the results of Partington[12] at 0° were similarly in error, particularly because when they were plotted a satisfactory curve was not obtained. Since it was probable that the same error was present in the determinations at 0 and at 25°, it appeared justifiable to calculate from the results the temperature coefficient of the conductance at the two temperatures. The ratio of the conductance at 0° to that at 25° was at 0.01 formal 0.7364, at 0.025 0.7266, at 0.05 7288, at 0.075 0.7406 and at 0.10 0.7333. The average was 0.7331. With the use of this factor the conductance of hydrogen chloride in ethyl alcohol at 0° was calculated from Goldschmidt's values at 25°. When the values thus obtained were used in subsequent calculations the results were found to be satisfactory.

On account of the fact that conductance determinations had been made at a relatively small number of concentrations it was impossible to construct accurately from the values a large scale curve to be used in determining concentrations from the observed conductances. A method of plotting suggested by Professor George Scatchard of the Research Laboratory of Physical Chemistry solved the difficulty. When the values of the square roots of the specific conductances were plotted against the ratios of the molality to the specific conductance a short curve was obtained that could be plotted accurately. First, a straight line was drawn through the points for the extreme values and the equation of the line calculated as $M/L = 0.01928 + 0.018945 \sqrt{L}$. For any point on the curve M/L equals the above value $+\Delta$. The values of Δ were calculated from the known ratios of M/L and used to obtain a smooth curve, which resembled a parabola, by plotting Δ against L. The values of Δ obtained from the curve were used in the equation $M/L = 0.01928 + 0.018945 \sqrt{L} + \Delta$ to calculate a table which contained the concentrations corresponding to a large number of specific resistances. By the use of this table it was possible to extrapolate accurately for intermediate concentrations to within 0.1%.

The reaction in each case was allowed to go to completion and the resistance taken as a measure of the original concentration. Since on long standing the resistance rose very slowly from a minimum, the latter was used in the calculations. The values of the *log* terms in the equation for the first order constant were plotted against times. The intersection of the straight line obtained with the time axis gave the corrected time. It was found more accurate to calculate from the observations the most probable points which determined the slope of the plotted line, and the corrected time. The constants calculated from these data at the different time intervals did not deviate more than 2.5% from the average constant throughout the average conversion range from 8 to 85%.

The constants for certain determinations were calculated from the concentrations obtained by weighing the acyl chloride and taking into account that the non-electrolyte present lowered the conductance (from 3 to 8%). Since the re-

TABLE III

FIRST ORDER VELOCITY CONSTANT *o*-BROMOBENZOYL CHLORIDE AND ETHYL ALCOHOL

Temp., 0°. Cell constant 1.0511. Ethyl alcohol 23.3717 g. (d^{25}_4 0.78510). *o*-Bromobenzoyl chloride 0.5248 g. Formality of solution, 0.1023. (1) Time acyl chloride ampule broken 4:11.4. (2) Time solution shaken, 12 sec. (3) Time solution put in cell, 4:12.6. (4) Observed time correction (3 − 1) + 1.2 m. (5) Calculated time correction (from probable points) + 1.9 m. (6) Calculated final specific conductance of solution 2.1584×10^{-3}. (7) Observed final specific conductance 2.0764×10^{-3}. (8) From 6 and 7, calculated percentage lowering due to 0.1 *F* non-electrolyte 3.7%

Observed time in minutes	Corrected specific resistance	Formality of HCl	K
2	4845	0.005248	0.01421
4	3552	.00836	.01522
6	2854	.01084	.01495
10	2100	.01566	.01473
15	1589	.02200	.01516
25	1177.0	.03192	.01476
50	790.3	.05236	.01486
100	584.9	.07624	.01498
200	500.4	.09278	.01512
320	484.5	.09667	
380	482.4	.09720	
440	481.6	.09740	

Ordinates of most probable points: T_1 (from 2 to 15 m.) = 8.14, $\log 1/(1 - x) = 0.06484$; T_2 (from 20 to 100 m.) = 55.86, $\log 1/(1 - x) = 0.3729$. Calculated average constant 0.01487. Max. deviation of constants from 9 to 93%, conversion 2.4%.

TABLE IV

FIRST ORDER VELOCITY CONSTANTS $RCOCl + C_2H_5OH$. TEMP., 0°. TIME IN MINUTES

The letters after the values indicate the observer, S = Staud, F = Fasce

Acyl chloride	M. p. or b. p., °C.	First order constant	Most probable value
C_6H_5COCl	78.8 (10.5 mm.) F	0.00485 S, 0.00468 S, 0.00442 S	0.0044
		.00451 F, .00437 F, .00436 F	
o-CH_3	101.6–101.7 (5 mm.) S	.0162 S, .0159 S	.0161
p-CH_3	220.2–220.3 S	.00342 S, .00327 S	.00335
p-CH_3O	M. p. 21.5–21.6 S	.00357 S, .00422	.0039
o-Cl	224–224.5 S	.0153 S, .0154 S, .0172 S	.016
p-Cl	221–221.5 S	.00807 S, .00832 S, .00866 S	.0084
o-Br	88–88.5 (1 mm.) F	.0146 F, .0149 F, .0148 F	.0149
m-Br	134–134.5 (10 mm.) S	.0201 S, .0212 S, .0203 S	.0202
	74.5–75 (0.5 mm.) F	.0202 F, .0202 F	
p-Br	127 (11 mm.) S		
	M. p. (38.7) S	.00964 S, .00911 S	.0094
o-NO_2	M. p. 19.90–19.95 F	.00947 F, .00950 F	.0095
m-NO_2	109.5–110 (18 mm.) S	.0924 S, .0844 S, .0909 S	
	M. p. 31.1 F	.0894 F, .0917 F	.090
p-NO_2	M. p. 71.5 F	.0932 S, .0936 S, .0949 S	
	71.7 S	.0951 F	.095
C_6H_5COCl (25°)	78.8 (10.5 mm.) F	.0484 S, .0470 F	.047

sults agreed within 1.5% with those obtained by the simpler method of calculation and the error was within the limit of accuracy of the observations, this method was not used.

In Table II are given as an example the observations made and the data from which the constant was calculated in the case of *o*-bromobenzoyl chloride. For brevity only a part of the observations are given.

Summary

1. The rates have been determined at which benzoyl chloride and certain of its substitution products react with ethyl alcohol at 0°.

2. A comparison is made of the relative effects of CH_3, CH_3O, Cl, Br, I and NO_2 in the ortho, meta and para positions in the acyl chlorides on the rates at which these compounds react with alcohol.

3. It is shown that the effect of these substituents in the benzoyl chlorides is opposite from the effect of the same substituents in the benzyl chlorides.

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The Reactivity of Atoms and Groups in Organic Compounds. XVII. The Effect of the Change in Reactant and of the Temperature on the Relative Reactivities of Certain Substitution Products of Benzoyl Chloride[1]

BY JAMES F. NORRIS AND HARLAND H. YOUNG, JR.

A critical examination of the work accomplished in the study of reactivity as measured by reaction velocity leads to the conclusion that the following factors are involved: (a) the chemical nature (as defined by negativity or electron affinity) of the carbon atom to which the reacting atom is bound, (b) the chemical nature of the atom or group which replaces the reactive atom, (c) the temperature, (d) the solvent in which the reaction takes place and (e) the presence of catalysts.

Only a few of these factors have been systematically investigated. In a previous paper[2] the relative reactivities of derivatives of benzyl chloride and of benzoyl chloride with ethyl alcohol were considered. The replacement of two hydrogen atoms in the benzyl chlorides by one

[1] From the thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy by Harland H. Young, Jr., 1932.

[2] Norris, Fasce and Staud, THIS JOURNAL, **57**, 1415 (1935).