

TABLE IV  
FIRST ORDER VELOCITY CONSTANTS  $\text{RCOCl} + \text{C}_2\text{H}_5\text{OH}$ . TEMP.,  $0^\circ$ . TIME IN MINUTES  
The letters after the values indicate the observer, S = Staud, F = Fasce

Acyl chloride	M. p. or b. p., $^\circ\text{C}$ .	First order constant	Most probable value
$\text{C}_6\text{H}_5\text{COCl}$	78.8 (10.5 mm.) F	0.00485 S, 0.00468 S, 0.00442 S .00451 F, .00437 F, .00436 F	0.0044
<i>o</i> - $\text{CH}_3$	101.6–101.7 (5 mm.) S	.0162 S, .0159 S	.0161
<i>p</i> - $\text{CH}_3$	220.2–220.3 S	.00342 S, .00327 S	.00335
<i>p</i> - $\text{CH}_3\text{O}$	M. p. 21.5–21.6 S	.00357 S, .00422	.0039
<i>o</i> -Cl	224–224.5 S	.0153 S, .0154 S, .0172 S	.016
<i>p</i> -Cl	221–221.5 S	.00807 S, .00832 S, .00866 S	.0084
<i>o</i> -Br	88–88.5 (1 mm.) F	.0146 F, .0149 F, .0148 F	.0149
<i>m</i> -Br	134–134.5 (10 mm.) S 74.5–75 (0.5 mm.) F	.0201 S, .0212 S, .0203 S .0202 F, .0202 F	.0202
<i>p</i> -Br	127 (11 mm.) S M. p. (38.7) S	.00964 S, .00911 S	.0094
<i>o</i> - $\text{NO}_2$	M. p. 19.90–19.95 F	.00947 F, .00950 F	.0095
<i>m</i> - $\text{NO}_2$	109.5–110 (18 mm.) S M. p. 31.1 F	.0924 S, .0844 S, .0909 S .0894 F, .0917 F	.090
<i>p</i> - $\text{NO}_2$	M. p. 71.5 F 71.7 S	.0932 S, .0936 S, .0949 S .0951 F	.095
$\text{C}_6\text{H}_5\text{COCl}$ ( $25^\circ$ )	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  $0^\circ$ .

2. A comparison is made of the relative effects of  $\text{CH}_3$ ,  $\text{CH}_3\text{O}$ , Cl, Br, I and  $\text{NO}_2$  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.

CAMBRIDGE, MASS.

RECEIVED MAY 11, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 124]

## 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<sup>1</sup>

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,

(1) From the thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy by Harland H. Young, Jr., 1932.

(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<sup>2</sup> 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

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

oxygen atom had a marked effect. The study of the effect on the reactivity produced by the substitution of a hydrogen in the ring in the two classes of compounds brought out the fact that the nature of the substituent and its position had opposite effects in the two series.

In this paper are given the first results of an investigation to study systematically the effect of (b) above, namely, the effect of the change in the chemical nature of the atom or group which replaces the chlorine atom in the acyl chlorides. The great significance of this factor has been largely overlooked. It appears highly probable that the relative reactivities of the C-Cl bonds in two compounds in which the carbon atoms differed greatly in electron affinity would be in a different order when measured by reactions as the result of which the chlorine atom is replaced in one case by an atom or group more negative than chlorine and in the other by an atom or group more positive than chlorine. The work of Conant and Hussey<sup>3</sup> indicates that this is the case when the C-Cl bonds in *n*-butyl chloride and *t*-butyl chloride are compared. When the reaction involves the replacement of chlorine by hydroxyl the tertiary compound is much more reactive; when the chlorine is replaced by iodine the normal chloride is the more reactive. Conant and co-workers<sup>4</sup> have also reported the relative rates at which certain substitution products of benzyl chloride react with potassium iodide. A comparison of these rates with those found by Olivier,<sup>5</sup> when the same compounds reacted with ethyl alcohol, shows that the order of the activation effect produced by the substituents is opposite in the two series; for example, *p*-nitrobenzyl chloride reacts with potassium iodide 6.6 times as fast as benzyl chloride reacts; with ethyl alcohol, the nitro derivative reacts 0.1 as fast as benzyl chloride. A study of such facts will increase our knowledge of chemical bonds and help in the interpretation of reactions through the use of the concept of electron valence.

In this paper are reported the relative rates at which a series of derivatives of benzoyl chloride react with methyl alcohol, and the results are compared with those previously obtained with ethyl alcohol. The significance of the change in the nature of the substance used in determining relative reactivities will be studied by using

radicals that differ in electron affinity to a much greater degree than that shown by the two alkoxyl groups considered here.

This paper also presents the results of the study of the influence of temperature on the relative reactivities of certain benzoyl chlorides when measured by ethyl alcohol at 0 and at 25°. The results make possible the calculation of the heats of activation and a consideration of the changes in these heats produced as the results of the introduction into different positions in the ring of radicals which possess widely different electron affinities.

A research is now in progress in this Laboratory on the combined effect of two or more like or unlike substituents on the reactivity of derivatives of benzoyl chloride. In this paper are given the results with tribromo-, trinitro- and trimethyl-benzoyl chloride; the substituents in each case were in the 2,4,6 positions. The nitro compound reacted with methyl alcohol at 25° so slowly that the rate could not be measured. The reaction between the methyl derivative and methyl alcohol at 0° was complete in less than thirty seconds; the reaction was so fast it could not be measured. The significance of these results and their bearing on steric hindrance will be considered in a later communication.

The conclusions drawn from the results can be arrived at from an examination of Table I in which the rates are given of the reactions between derivatives of benzoyl chloride and methyl and ethyl alcohols. The numbers are obtained from first order velocity constants.

TABLE I  
REACTION VELOCITY CONSTANTS

I Acyl chloride	REACTION VELOCITY CONSTANTS				
	II $K^{Me} \times 10^2$	III $K_0^{Et} \times 10^2$	IV $K_0^{Me}/K_0^{Et}$	V $K_{25}^{Et} \times 10^2$	VI $K_{25}^{Et}/K_0^{Et}$
Benzoyl	2.65	0.44	6.02	4.7	10.8
<i>o</i> -CH <sub>3</sub>	13.7	1.61	8.41	20.9	12.8
<i>m</i> -CH <sub>3</sub>	2.95	0.375	7.87	4.72	12.6
<i>p</i> -CH <sub>3</sub>	1.78	.335	5.2	3.35	9.8
<i>o</i> -Cl	7.41	1.60	4.81	12.6	8.2
<i>m</i> -Cl	8.88	2.46	3.61	15.4	6.3
<i>p</i> -Cl	4.31	0.84	5.16	7.24	8.7
<i>o</i> -Br	7.33	1.49	4.95	...	..
<i>m</i> -Br	9.25	2.02	3.99	...	..
<i>p</i> -Br	4.81	0.94	5.12	...	..
<i>o</i> -NO <sub>2</sub>	4.72	.95	4.97	7.30	7.7
<i>m</i> -NO <sub>2</sub>	32.8	9.0	3.61	...	..
<i>p</i> -NO <sub>2</sub>	41.3	9.5	4.42	...	..
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	1.98	..	...	...	..

An examination of columns II and III in Table I brings out the fact that two kinds of con-

(3) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

(4) Conant, Kirner and Hussey, *ibid.*, **47**, 488 (1925).

(5) Olivier, *Rec. trav. chim.*, **49**, 996 (1930).

clusions can be drawn, namely, (a) those in which the two alcohols yield similar results and (b) those in which the results are different.

(a) If the acyl chlorides are arranged according to increasing reaction velocities, the order in the two series is the same with the exception of one striking difference, which is discussed in (b) below.

The relative rates are affected by the two important factors noted below. In order to discover these a comparison should be made between different substituents in the same position and the same groups in different positions. When such a comparison is made the two alcohols yield similar results.

The relation between the nature of the group and its position is shown in Table II.

TABLE II  
EFFECT OF GROUP AND POSITION ON RELATIVE VELOCITIES

Measured by	Substituent			
	CH <sub>3</sub>	Cl	Br	NO <sub>2</sub>
	Ortho Position			
CH <sub>3</sub> OH at 0°	13.7	7.41	7.33	4.72
C <sub>2</sub> H <sub>5</sub> OH at 0°	1.61	1.60	1.49	0.95
	Meta Position			
CH <sub>3</sub> OH at 0°	2.95	8.88	9.25	32.8
C <sub>2</sub> H <sub>5</sub> OH at 0°	0.37	2.46	2.02	9.0
	Para Position			
CH <sub>3</sub> OH at 0°	1.78	4.31	4.81	41.3
C <sub>2</sub> H <sub>5</sub> OH at 0°	0.34	0.84	0.94	9.5

It is seen from Table II that the two alcohols yield similar results. In the ortho position the methyl radical has the greatest influence and the nitro group the least. In the para position the order is reversed. In the meta position the order when measured by methyl alcohol is the same as in the para position; when measured by ethyl alcohol the activating influences of Cl and Br are reversed—a fact considered later.

If the effect of position on the activating influence of a particular atom or group is compared by the use of either alcohol, similar results are obtained in the two cases. In the case of CH<sub>3</sub> the order is *o* > *m* > *p*, the effect in the ortho position being pronounced. In the case of NO<sub>2</sub> the order is *p* > *m* > *o*, with large effects in the para and meta positions. With Cl and Br the order is *m* > *o* > *p*. These facts are significant and show the great effect of the position of a substituent and that this effect can largely overcome the effect of the electron affinity of the substituent. In all the results the great difference between the methyl radical and the nitro group is clear, not only in re-

gard to electron affinity but also in regard to position. In general the effects are opposite.

(b) The differences in relative velocities when the latter are measured by the replacement of the chlorine atom by methoxyl and by ethoxyl are of particular interest. It is probable that the conclusions drawn in (a) were possible because the factors involved were of such magnitudes that general relations between the reactivities could be deduced.

In IV of Table I are given numbers which show the relationship between the velocity constants with methyl alcohol and with ethyl alcohol at 0°. The effect produced by a change in the reactant is great and differs with the several acyl chlorides. The change from ethyl alcohol to methyl alcohol increases the rate, for example, with benzoyl chloride 6 times, with the *o*-CH<sub>3</sub> derivative 8.4 and with *m*-NO<sub>2</sub> 3.6 times. The greatest percentage differences in relative reactivities are seen in the case of the more rapid reactions. The CH<sub>3</sub> radical in the *ortho* position has a greater activating effect when the chlorine is replaced by methoxyl than when replaced by ethoxyl. The relationship is reversed when the substituent is the NO<sub>2</sub> group; the greatest effects are in the meta and para positions and the ethoxyl group produces greater reactivity than the methoxyl group. All the chlorine, bromine and nitro derivatives have greater relative reactivities when the acyl chlorine atom is replaced by ethoxyl; both the ortho and meta derivatives containing CH<sub>3</sub> have greater relative reactivities when the replacement is by methoxyl. It seems probable that these differences result from the change produced by substituents in the ring on the electron affinity of the carbon atom to which the reacting chlorine atom is joined in the acyl chlorides. This subject will be discussed more fully in a subsequent paper.

It was stated above that if all the compounds studied are listed according to decreasing reactivity when measured by methyl alcohol and by ethyl alcohol the order is the same, with one significant exception. The positions of the *o*-CH<sub>3</sub> and *m*-Cl compounds are reversed in the two series. The reactivities of these acyl chlorides are greatly affected by a change from CH<sub>3</sub>O to C<sub>2</sub>H<sub>5</sub>O as the entering group and the effects produced are in different directions.

The only exception to the effect of position on reactivity as shown in Table II is the reversal of

the effect of chlorine and bromine in the meta position. When measured by methyl alcohol the effect of the halogens is that produced by the nitro group—Br > Cl. With ethyl alcohol the order is Cl > Br, which is similar to the effect produced by the methyl radical. The halogens stand between the extremes, CH<sub>3</sub> and NO<sub>2</sub>; in most cases they resemble the NO<sub>2</sub> group but in a few, the CH<sub>3</sub> radical. Facts of this kind, when small differences produce opposite effects, will be valuable in checking up on the value of a hypothesis which aims to interpret the facts through the concept of electron affinity.

**The Effect of Temperature on Relative Reactivities.**—It has been recognized for a long time that the relative rates at which the members of a series of analogous compounds react with a fixed reagent at a fixed temperature were significant only under the experimental conditions used. The effect of the change in the fixed reagent has been discussed above. With change in temperature the relative reactivities would remain constant only when the temperature coefficients of the several reactions had the same value. To determine the effect of change in temperature on the relative reactivities of the acyl chloride the rates at 25° with ethyl alcohol were measured. The rates are given in column V and the ratio between the rates at 25 and 0° in column VI of Table I.

The great difference in the effect of temperature on the reactions is striking. From the columns V and VI there appears to be no relation between the temperature coefficients (or the calculated heats of activation) and the rates of the reactions. A comparison of the ortho and the meta methyl derivatives shows that the rates can be very different although the temperature coefficients have nearly the same value. If the *o*-CH<sub>3</sub> and the *m*-Cl derivatives are compared it is seen that the faster reaction has the greater temperature coefficient; in the case of the *m*-Cl and *p*-Cl derivatives the faster reaction has the lower temperature coefficient.

There appears to be, however, a relationship between temperature coefficients and the nature of the substituent and its position. The methyl derivatives have the highest coefficients and the greatest effect is in the ortho position—*o* > *m* > *p*. The compounds containing chlorine and the nitro group have much lower coefficients; the highest in the case of Cl is in the para position—*p* > *o* > *m*. It is a striking and perhaps significant fact that

the change in the relative reactivities produced by rise in temperature which increases the velocities of all the reactions is in the same order as the change in reactivities produced by increasing the rates by the substitution of methyl alcohol for ethyl alcohol. A comparison of columns IV and VI shows this to be the case.

It is evident in the cases reported here that the increases in rates produced by the introduction of heat energy into the various systems bear no relation to the original rates. The increase in rate in any case is determined by the nature of the substituent and its position. The compounds containing CH<sub>3</sub> (and in all probability radicals similar to CH<sub>3</sub> in electron affinity) are greatly influenced by rise in temperature; the presence of halogen atoms and the nitro group leads to greatly reduced response to changes in temperature.

#### Experimental Details

The methods of measuring and calculating the reaction velocities were the same as those described in detail in the paper by Norris, Fasce and Staud. The values of the conductance of hydrogen chloride in ethyl alcohol at 0 and at 25° were those used in the earlier investigation. The values of Goldschmidt and Dahll<sup>6</sup> for the conductance of hydrogen chloride in methyl alcohol at 25° were used. These were checked at a number of concentrations and the conductances of the same solutions determined at 0°. The results made it possible to plot a curve for the conductance at 0°. The conductance at 0° divided by the conductance at 25° changed in a smooth curve from 0.7796 at 0.12738 (wt. mol.) to 0.07500 at 0.000995 (wt. mol.).

The alcohols used were carefully purified and protected from the air. The three samples of ethyl alcohol used had the following densities at 25/4°: 0.78509, 0.78506, 0.78507. The value given by Brunel is 0.78505. The density of the methyl alcohol was 0.7883 and 0.7885 at 25/4°.

The acyl chlorides were prepared by the action of thionyl chloride on recrystallized acids which gave constant melting points. The chlorides were distilled at reduced pressures or recrystallized from carbon tetrachloride, petroleum ether or a mixture of the two. The boiling or melting points of the compounds used are given in Table III. The values are not repeated in the table when a chloride was used for several reactions.

(6) Goldschmidt and Dahll, *Z. physik. Chem.*, **106**, 121 (1924).

TABLE III  
FIRST ORDER VELOCITY CONSTANT (TIME IN MINUTES)  
RCOCl + CH<sub>3</sub>OH at 0°

Acyl chloride	M. p. or b. p., °C.	Constant		Most probable value
C <sub>6</sub> H <sub>5</sub> COCl	77.9-78.0 (8 mm.)	0.0260	0.0269	0.0265
<i>o</i> -CH <sub>3</sub>	75.0-75.5 (2 mm.)	.137	.137	.137
<i>m</i> -CH <sub>3</sub>	-25; 119-120 (36 mm.)	.0294	.0295	.0295
<i>p</i> -CH <sub>3</sub>	90-90.5 (3 mm.)	.0177	.0178	.0178
<i>o</i> -Cl	224 (at.)	.0741	.0740	.0741
<i>m</i> -Cl	77.5-78 (1 mm.)	.0877	.0889	.0888
<i>p</i> -Cl	79.5-79.7 (2 mm.)	.0432	.0430	.0431
<i>o</i> -Br	100-101 (1 mm.)	.0737	.0729	.0733
<i>m</i> -Br	74.5-75 (0.5 mm.)	.0917	.0932	.0925
<i>p</i> -Br	108-108.5 (1 mm.)	.0486	.0482	.0481
<i>o</i> -NO <sub>2</sub>	19.90-19.95 (m. p.)	.0475	.0470	.0472
<i>m</i> -NO <sub>2</sub>	33-33.5 (m. p.)	.328	.328	.328
<i>p</i> -NO <sub>2</sub>	71.5-71.7 (m. p.)	.416	.410	.413
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	111 (m. p.)	.0214	.0183	.0198
2,4,6-tri-CH <sub>3</sub>	85-85.5 (4 mm.)	Too fast to measure		
RCOCl + CH <sub>3</sub> OH at 25°				
C <sub>6</sub> H <sub>5</sub> COCl		0.253	0.259	0.256
2,4,6-tri-Br	45.4-46 (m. p.)	.000186		
2,4,6-tri-NO <sub>2</sub>	158-158.5 (m. p.)	Too slow to measure		
RCOCl + C <sub>2</sub> H <sub>5</sub> OH at 0°				
<i>m</i> -CH <sub>3</sub>		0.00367	0.00383	0.00375
<i>o</i> -CH <sub>3</sub> O	105-106 (1 mm.)	.126	.127	.127
<i>m</i> -CH <sub>3</sub> O	81.5-82 (1 mm.)	.00464	.00457	.00461
<i>m</i> -Cl		.0246	.0245	.0246
<i>o</i> -I	36-37; 105-106 (1 mm.)	.0125	.0129	.0127
<i>m</i> -I	104-105 (1 mm.)	.179	.0190	.0179
<i>p</i> -I	78.5-79; 120-121 (1 mm.)	.00827	.00842	.0083
RCOCl + C <sub>2</sub> H <sub>5</sub> OH, 25°				
<i>o</i> -CH <sub>3</sub>		0.210	0.208	0.209
<i>m</i> -CH <sub>3</sub>		.0475	.0469	.0472
<i>p</i> -CH <sub>3</sub>		.0368	.0345	
		.0307	.0320	.0335
<i>o</i> -Cl		.125	.126	.126
<i>m</i> -Cl		.153	.155	.154
<i>p</i> -Cl		.0721	.0726	.0724
<i>o</i> -NO <sub>2</sub>		.0736	.0724	.0730

On account of the extreme rapidity with which the 2,4,6-trimethylbenzoyl chloride reacted with methyl alcohol the compound was studied further

to establish its identity. The methyl ester prepared from it boiled at 101-102° at 3 mm. and was shown to be identical with a sample of the ester prepared from methyl iodide and the silver salt of the corresponding acid. The index of refraction of the latter was 1.4970 and of the former 1.4969. The acid made from the acyl chloride melted at 188-188.5°; Hantzsch and Lucas<sup>7</sup> give 187-188°. Analyses of the chloride by the Carius method gave 19.38 and 19.30% Cl; theoretical 19.42% Cl.

### Summary

1. The first order velocity constants have been determined of the reactions between certain substituted benzoyl chlorides and ethyl alcohol at 0 and 25°, and methyl alcohol at 0°.

2. The effect on the relative velocities produced by measuring the reactivities with the two alcohols is discussed.

3. The temperature coefficients of the reactions bear no relationship to the rates, but can be correlated with the nature of the substituent and its position.

4. Three trisubstituted derivatives have been studied. 2,4,6-Trinitrobenzoyl chloride reacted with methyl alcohol so slowly the rate could not be measured; the rate with the 2,4,6-tribromo compound was very slow but measurable; 2,4,6-trimethylbenzoyl chloride reacted so rapidly the rate could not be measured.

CAMBRIDGE, MASS.

RECEIVED MAY 11, 1935

(7) Hantzsch and Lucas, *Ber.*, **28**, 748 (1895).