hydrolysis of the semicarbazone during the titration. By this means the rates of semicarbazone formation of a variety of carbonyl compounds, some of them of relativly high reactivity, have been measured with sufficient precision to permit reliable determination of the effect of structure of carbonyl compound upon heat and entropy of activation.

The potential energy barrier opposing the formation of the transition state is of nearly the same height for acetone, diethyl ketone and pinacolone, and the ninety-fold variation in rate of reaction is essentially an entropy effect. The same consideration applies to the thirty-fold difference in rate between acetophenone and furfural.

On the other hand, there is a difference of well over 2000 cal. in the barrier height in the series cyclopentanone, acetone, cyclohexanone, for which no satisfactory explanation seems to be available. The similar difference in barrier height between acetone and acetophenone is no doubt due to resonance stabilization of the latter ketone.

For all the compounds studied the entropy of activation increases with increasing rigidity of the structure of the carbonyl compound, an effect for which an explanation is offered.

A thermostat of new design wherein temperatures around 0° can be obtained to a constancy of ±0.002° is described.

NEW YORK, N. Y. RECEIVED MAY 23, 1941

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

# Esterification Kinetics of Disubstituted Benzoic Acids in Methyl Alcohol

BY A. G. GASSMANN[1] AND R. J. HARTMAN

Investigations of the esterification of substituted benzoic acids have been carried out by Kellas,[2] Goldschmidt,[3] Sudborough and Turner,[4] Hinshelwood,[5] Hartman,[6] and others. The effect of substituents on the reaction velocity of various compounds has been explained in theories presented by Williams[7] and by Hammett.[8] Williams classified reactions into three groups according to the electronic shift toward or away from the point of reaction. The effect on the reaction velocity of a meta or para substituent on the benzene ring is expressed by the Hammett[8] equation

$$\log k = \log k_0 + \rho\sigma$$

where $k$ is the velocity constant of the substituted reactant, $k_0$ the velocity constant of the unsubstituted reactant, $\rho$ a constant depending on the reaction, medium, and temperature, and $\sigma$ a constant depending upon the substituent. A prediction of the reaction rate of esterification of substituted benzoic acids is possible if the value of the substituent constant, $\sigma$, is known. Hammett[8] has determined values of $\sigma$ for many mono-substituents from the data of Dippy.[9] However, no values of $\sigma$ are given for the dichloro and dinitro substituents.

Since the investigations cited above are concerned primarily with mono-substituents, it is not possible to predict the velocities of the reactions of disubstituted compounds. The object of this investigation was to determine the velocity of esterification of 2,4-DiCl, 2,5-DiCl, 3,5-DiCl and 3,5-$DiNO_2$ benzoic acids with methyl alcohol and catalyzed by hydrions. From these data, the energies of activation of the reactions were determined, thus enabling an analysis of the results from the standpoint of the Arrhenius equation.

## Experimental

**Materials.**—Absolute methanol was purified by the method of Bjerrum and Lund[10] with magnesium methylate. Water, aldehyde, and ketone tests were negative. The acids were obtained either from Eastman Kodak Company or from Professor C. S. Marvel of the University of Illinois. The melting points of the purified acids were as follows:

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(1) This paper represents a part of a thesis presented by Albert George Gassmann to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Kellas, *Z. physik. Chem.*, **24**, 221 (1897).

(3) Goldschmidt, *et al.*, *ibid.*, **60**, 728 (1907); **61**, 30 (191); **143**, 139 (1929).

(4) Sudborough and Turner, *J. Chem. Soc.*, **101**, 237 (1912).

(5) Hinshelwood, *et al.*, *Trans. Faraday Soc.*, **30**, 935, 1145 (1934); *J. Chem. Soc.*, 587, 1588 (1935).

(6) Hartman, *et al.*, THIS JOURNAL, **59**, 2107 (1937); **61**, 2167 (1939); **62**, 1559 (1940).

(7) Williams, *J. Chem. Soc.*, 37 (1937).

(8) Hammett, THIS JOURNAL, **59**, 97 (1937).

(9) Dippy, *J. Chem. Soc.*, 644 (1936).

(10) Bjerrum and Lund, *Ber.*, **B64**, 210 (1931).

| Acid | M. p., °C. |
|---|---|
| 2,4-Dichlorobenzoic | 161.5–162.5 |
| 2,5-Dichlorobenzoic | 153.0–153.5 |
| 3,5-Dichlorobenzoic | 184.0–185.0 |
| 3,5-Dinitrobenzoic | 203.5–204.5 |

**Procedure.**—The procedure followed was similar to that of Hartman and Borders.[11] The acids were dried over phosphorus pentoxide preceded in certain instances by drying in an oven at 105–110°. The total acid concentration was determined at the beginning and at intervals throughout the course of the reaction by titrating 5-ml. samples with barium hydroxide solution using phenolphthalein as indicator. The constant temperature baths were maintained at 30.00, 40.00, 50.00 and 60.00 ± 0.02°.

## Results and Discussion

The value of the velocity constant which accounts for the retardation of the reaction due to the water formed is given by the equation[12]

$$k = \frac{(r + a)\ln\left[\dfrac{a}{a - x}\right] - x}{crt}$$

where $r$ is a constant which compensates for the water formed, $a$ the initial organic acid concentration, $x$ the quantity of acid esterified in time $t$, $c$ the concentration of the hydrion catalyst, and $k$ the velocity constant in g. moles/liter/sec. The value of $r$ is dependent for any given temperature[13] only upon the alcohol and not upon the acid. The values of $r$ used were[11,13,14]

| Temp., °C. | 30 | 40 | 50 | 60 |
|---|---|---|---|---|
| $r$ | 0.26 | 0.36 | 0.42 | 0.56 |

The application of the Goldschmidt equation[12] to a typical esterification reaction is shown in Table I. The units of the velocity constants are g. moles/liter/sec. The given values of $(a - x)$ and of $k$ represent averages of several runs.

TABLE I

ESTERIFICATION OF 2,4-DICHLOROBENZOIC ACID AND METHANOL AT 40°

$a = 0.0898$, $c = 0.0391$

| Time, min. | $a - x$ | $10^4k$ |
|---|---|---|
| 570 | 0.0758 | 1.29 |
| 1410 | .0611 | 1.20 |
| 2055 | .0503 | 1.26 |
| 2985 | .0380 | 1.32 |
| 4245 | .0268 | 1.33 |
| 6900 | .0151 | 1.25 |
| | | Av. 1.27 |

Only those values of $k$ which represent between 20 and 80% reaction are reported since errors owing to hydrolysis effects, etc., are apparent at the beginning and end of a reaction. Table II gives the velocity constants and energies of activation for the acids studied in this investigation. The values of the activation energies, $E$, were obtained graphically from the slope of the line obtained by plotting log $k$ against the reciprocal of the absolute temperature. The points thus plotted are found to yield smooth curves, within narrow limits of experimental error.

TABLE II

VELOCITY CONSTANTS AND ENERGIES OF ACTIVATION FOR HYDRION CATALYZED ESTERIFICATION OF DISUBSTITUTED BENZOIC ACIDS WITH METHYL ALCOHOL

| | $10^4k$ | | | | Energy of activation, $E$ |
|---|---|---|---|---|---|
| Acid | 30° | 40° | 50° | 60° | |
| 3,5-Dinitrobenzoic | 0.333 | 0.837 | 1.73 | 3.50 | 15,500 |
| 2,4-Dichlorobenzoic | .458 | 1.27 | 3.25 | 7.10 | 18,300 |
| 2,5-Dichlorobenzoic | .535 | 1.17 | 2.36 | 4.75 | 14,500 |
| 3,5-Dichlorobenzoic | .808 | 2.16 | 5.48 | 12.28 | 18,100 |

The data of Table II show that at 60° 2,4-dichlorobenzoic acid is esterified more rapidly than 2,5-dichlorobenzoic acid. At 30°, however, the velocity of esterification of 2,5-dichlorobenzoic acid is the greater. The increase in the velocity of the esterification of 2,4-dichlorobenzoic acid at the higher temperature is indicated by a higher energy of activation. Hartman and Borders[11] found that benzoic acid with an energy of activation higher than *m*-toluic acid was esterified more rapidly at 60° than the *m*-toluic acid. At 25°, however, *m*-toluic acid was esterified more rapidly than benzoic acid. Hartman, Storms and Gassman[15] found that *m*-bromobenzoic acid had a higher energy of activation and was esterified more rapidly at 75° than *m*-chlorobenzoic acid. However, *m*-chlorobenzoic acid was esterified more rapidly at 55°.

The non-exponential factor, $P$, of the Arrhenius equation

$$k = PZe^{-E/RT}$$

has been considered to have significant variation in the bromination of substituted acetophenones according to Evans, Morgan and Watson.[16] However, the relatively narrow range of velocities studied by them has caused Nathan and Ingold[17] to question their accurate separation of the factors $E$ and $P$. Since the velocity range of the acids studied in the present investigation is also

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(11) Hartman and Borders, THIS JOURNAL, **59**, 2107 (1937).

(12) Goldschmidt and Udby *Z. physik. Chem.*, **39**, 711 (1906).

(13) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

(14) Smith and Reichardt, THIS JOURNAL, **63**, 605 (1941).

(15) Hartman, Storms and Gassmann, *ibid.*, **61**, 2167 (1939).

(16) Evans, Morgan and Watson, *J. Chem. Soc.*, 1168 (1935).

(17) Nathan and Ingold, *ibid.*, 222 (1936).

limited, it is not possible to study quantitatively the data from the point of view of the Arrhenius equation.

An approximation of the change in the factors of the Arrhenius equation may be obtained by plotting the values of the energies of activation, $E$, against log $k$ at 30°. This relationship is shown in Fig. 1. The broken line having a slope of $2.303RT$ is included since the acids would lie on a line of this slope if their velocity constants were entirely dependent on $E$. From the data given it is apparent that the factor $P$ varies since the solid lines do not have a slope of $2.303RT$.

Further investigation of the kinetics of esterification of polysubstituted benzoic acids is being conducted.

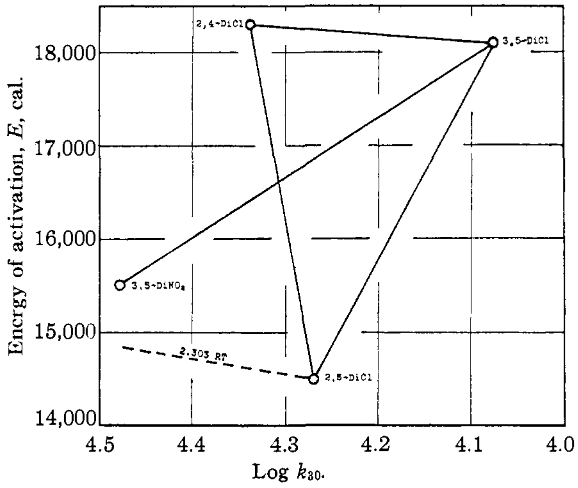

Fig. 1.—Relationship between reaction velocity and activation energy.

## Summary

The velocity constants and energies of activation of 2,4-dichlorobenzoic acid, 2,5-dichlorobenzoic acid, 3,5-dichlorobenzoic acid and 3,5-dinitrobenzoic acid have been determined.

The velocity of esterification is apparently affected by both the $P$ factor of the Arrhenius equation and $E$, the energy of activation.

BLOOMINGTON, INDIANA RECEIVED APRIL 26, 1941

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Kinetics of the Photochemical Formation of Phosgene

BY PAUL M. FYE AND J. J. BEAVER[1]

## Introduction

The various investigations concerning the photochemical formation of phosgene from carbon monoxide and chlorine have included the development of possible mechanisms explaining the accumulated data. At present there are two mechanisms—both of which on final analysis give the observed over-all rate equation—which must be given consideration. First that originating with Bodenstein[2] and his co-workers for room temperature and total pressures ranging from 200 to 600 mm. of mercury is given as

$$Cl_2 + h\nu \longrightarrow 2Cl \quad (1)$$
$$Cl + CO + M \longrightarrow COCl + M \quad (2)$$
$$COCl + M \longrightarrow CO + Cl + M \quad (2a)$$
$$COCl + Cl_2 \longrightarrow COCl_2 + Cl \quad (3)$$
$$COCl + Cl \longrightarrow CO + Cl_2 \quad (4)$$

It is assumed that an equilibrium concentration of the free radical (COCl) is established and maintained by equations (2) and (2a) and that reactions (3) and (4) are too slow to prevent the maintenance of this equilibrium. If it is also supposed in the customary manner that a fixed concentration of chlorine atoms is maintained, the following empirical rate equation may be derived

$$\frac{d(COCl_2)}{dt} = \frac{k_3 K_{COCl}{}^{1/2}}{k_4{}^{1/2}} I_a{}^{1/2}(Cl_2)(CO)^{1/2} \qquad (I)$$

$k_3$ and $k_4$ are the specific reaction rate constants for (3) and (4), $K_{COCl}$, the equilibrium constant for $CO + Cl \rightleftarrows COCl$, equals $k_2/k_{2a}$, and $I_a$ is the light absorbed by the reacting gases.

The chain-breaking process above is reaction (4); however, at total pressures below 20 mm. of mercury it is assumed to be

$$Cl \longrightarrow \text{wall} = {}^1/_2Cl_2 \qquad (5)$$

When (5) has completely replaced (4) the rate equation becomes

$$\frac{d(COCl_2)}{dt} = \frac{2k_3K_{COCl}}{k_5} I_a(Cl_2)(CO) \qquad (II)$$

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[1] Excerpt from the thesis submitted by Paul M. Fye to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1939.

[2] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929); Bodenstein, *Helv. Chim. Acta*, **18**, 743 (1935); Bodenstein, *Naturwissenschaften*, **23**, 10 (1935).