electrons toward the positively charged chlorine and away from the negatively charged catalyst particle; subsequent transfer of two electrons from the oxygen to the chlorine would result in the rupture of the oxygen–chlorine bond. In the activated complex the oxygen atom would probably share electrons with the catalyst surface; this unstable complex may then decompose as shown by equation 2, or combine with chloride ion to form the reactants again. The oxygen atom liberated in reaction (2) reacts very rapidly either with another oxygen atom to form molecular oxygen, or it may react with hypochlorite ion to form other products, for example, chlorate.

For unimolecular reactions, it is generally assumed that the rate of change of concentration of the activated complex is zero. If reaction (2) is very rapid, the concentration of activated complex is very small, and the steady state equation for the activated complex is

$$d[X^-]/dt = k_1[OCl^-][C^-] - k_{-1}[X^-][Cl^-] - k_2[X^-] = 0$$

Solving for the concentration of activated complex

$$[X^-] = \frac{k_1[OCl^-][C^-]}{k_{-1}[Cl^-] + k_2}$$

The chloride ion concentration of the solution is essentially constant, hence

$$k_{-1}[Cl^-] = k'_{-1}$$

and

$$[X^-] = \frac{k_1[C^-][OCl^-]}{k'_{-1} + k_2}$$

The rate of reaction is given by

$$-\frac{d[OCl^-]}{dt} = k_2[X^-] = \frac{k_1k_2[C^-][OCl^-]}{k'_{-1} + k_2}$$

But $[C^-]$, the amount of catalyst in the system, is essentially constant, therefore

$$\frac{k_1k_2[C^-]}{k_{-1} + k_2} = k', \text{ and } -\frac{d[OCl^-]}{dt} = k'[OCl^-]$$

which is the usual expression for first-order reaction rate.

In Table VIII it was shown that for phosphate buffered solution, the specific rate constant decreased with increasing hypochlorite concentration. This increased concentration of hypochlorite is accompanied by a proportional increase in chloride concentration, because these substances are formed in equi-molecular amounts in the preparation of the hypochlorite solution. The rate constant, k', used in the above expression, should be inversely proportional to the chloride ion concentration. If the rate controlling step were the formation of the activated complex, a plot of the reciprocal of the rate constant against the chloride ion concentration should be a straight line. Except for the highest concentration (Table VIII), this appeared to be approximately the case.

It was stated above that the oxygen atom liberated by reaction (2) might react with hypochlorite to form other products. Experimentally, it was known that beside oxygen and chloride ion, the principal product was chlorate ion. The formation of chlorate from hypochlorite is generally considered to give rise to second or third-order kinetics. The authors propose that in the system used in this study, the formation of chlorate can originate by first-order kinetics, by the mechanism of reactions (1) and (2) previously given, and

$$O + OCl^- \longrightarrow ClO_2^- \qquad (3)$$

The chlorite thus formed may react in either of two ways to form chlorate

$$ClO_2^- + O \longrightarrow ClO_3^- \qquad (4)$$

$$\text{or } ClO_2^- + OCl^- \longrightarrow ClO_3^- + Cl^- \qquad (5)$$

This mechanism would account for the observed catalysis of the disproportionation reaction, and would lead to first-order kinetics, since the over-all rate of disappearance of hypochlorite would be limited by the rate of formation of the activated complex which subsequently decomposed to form oxygen atoms.

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Kinetics of the Racemization of α-Phenethyl Chloride in Phenols

BY HAROLD HART AND WILLIAM L. SPLIETHOFF

RECEIVED AUGUST 11, 1954

The rates of racemization of α-phenethyl chloride in benzene or xylene solutions containing phenol, *o*- and *p*-cresol, 2,6-xylenol and mesitol were measured at 50°. The rates of the concurrent nuclear alkylation of the first four of these phenols were also determined using *dl*-chloride. The kinetic equation which fits the racemization data requires three simultaneous racemization paths; racemization brought about by the original phenol, by its alkylation product and by the hydrogen chloride evolved during the alkylation. The activation energy and entropy for the racemization and alkylation in phenol (30 to 50°) were determined. The mechanisms are discussed.

Studies on the racemization of α-phenethyl chloride have been important in developing the theory of displacement and elimination reactions. α-Phenethyl chloride racemizes at a measurable rate in polar solvents such as liquid sulfur dioxide[1] and formic acid,[2] more rapidly in the latter. The rate in sulfur dioxide was unaffected by excess chloride ion, indicating an ionization mechanism. Hughes, Ingold and Scott suggested[3] a reversible equilibrium with styrene and hydrogen chloride as a possible racemization path. The racemization with metallic halides in non-polar solvents has been studied recently[4] because of the interest in these halides as

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[1] E. Bergmann and M. Polanyi, *Naturwiss.*, **21**, 378 (1933).

[2] K. Bodendorf and H. Bohme, *Ann.*, **516**, 1 (1935).

[3] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1271 (1937).

[4] K. Heald and G. Williams, *ibid.*, 362 (1954).

ionic catalysts for the polymerization of styrene. Here, the mechanism is presumed to involve ionization, facilitated by complex ion formation.[2,4]

We recently noted[5] in a study of the stereochemistry of aromatic alkylation that, simultaneously with the alkylation, α-phenethyl chloride was racemized at a fairly rapid rate in the presence of phenols. It is the purpose of this paper to present a kinetic study and interpretation of this racemization.

Experimental

Materials.—Optically active α-phenethyl chloride was prepared[6] from the alcohol.[7] The phenols were commercial materials purified by distillation or recrystallization, except mesitol, which was synthesized from mesidine,[8] and recrystallized from petroleum ether, m.p. 68–69°. The solvents (benzene and *p*-xylene) were distilled from sodium, center cuts being used.

Kinetic Procedures. A. The Alkylation Reaction.—To ampoules maintained at −80° there was charged 2 ml. each of 5.0 *M* solutions of phenol and *dl*-α-phenethyl chloride in benzene or *p*-xylene. The ampoules were evacuated, sealed and placed in a bath at the desired temperature (usually 50.0 ± 0.1°). The reactions were sufficiently slow that the error in zero time (until temperature equilibrium was established) was not serious. The ampoules were shaken to ensure homogeneity. At various time intervals, samples were withdrawn from the bath, and the reaction quenched by cooling to −80°. Occasionally, duplicate samples were withdrawn, and complete duplicate runs were also made.

The reaction was followed by an analytical method which will be described in detail elsewhere. In principle, it consisted in extracting the phenols from the reaction mixture with alkali, liberation of the phenols by acidification, dilution with 60% aqueous methanol, and treatment of an aliquot with excess bromate–bromide, acid, potassium iodide and titration of the liberated iodine with thiosulfate. The amount of alkylated phenol present was calculated from the appropriate simultaneous equations, since it had fewer nuclear positions available for bromination than the starting phenol. Conditions which minimized side-chain bromination, and which corrected for the deviation of the alkali extraction from 100% efficiency were established. In some cases, aliquots of the diluted reaction mixture were used directly, after it was demonstrated that unreacted α-phenethyl chloride did not interfere with the determination. The analytical procedures were carefully tested on known mixtures, and gave good results. Dialkylation was shown to be insignificant, at least up to 70% reaction.

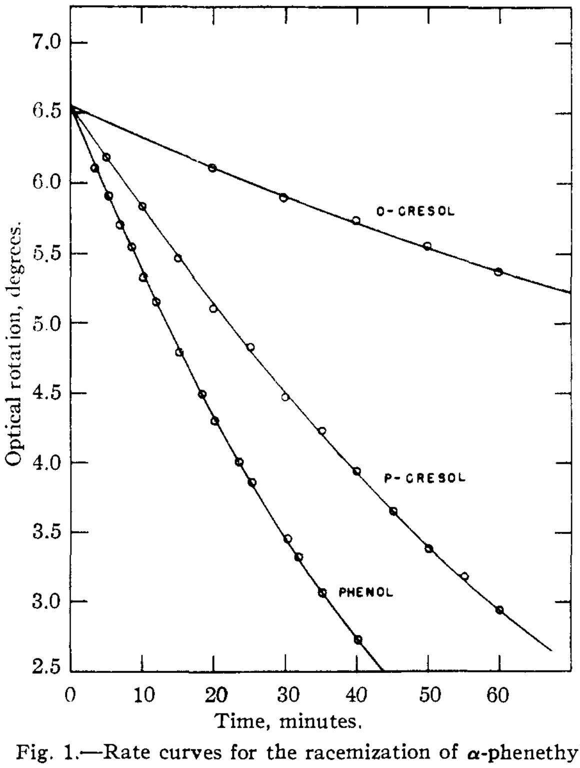

Fig. 1.—Rate curves for the racemization of α-phenethyl chloride in several phenols at 50°. The solid lines were calculated from equation 7.

B. The Racemization Reaction.—Solutions (5.0 *M*) of the phenol and optically active α-phenethyl chloride in *p*-xylene were thermostated at 50.0°. A 5-ml. portion of each solution was added to a 1-dm. jacketed polarimeter tube, also maintained at 50.0 ± 0.1° by circulating water; the tube was stoppered tightly, and rotations ±0.02° were determined on a Rudolph polarimeter at various time intervals. The time of mixing was taken as zero time, and the first reading was obtained within two minutes. Duplicate runs were made. In a control experiment, a 2.50 *M* solution of (+)-α-phenethyl chloride in *p*-xylene at 50.0° showed no change (±0.02°) in rotation in 36 hours.

Results

Racemization data were obtained as the over-all loss in optical activity with time. Some of this loss was due to disappearance of active chloride *via* the alkylation reaction. It was therefore necessary to determine the rates of the alkylation reaction with the several phenols studied.

Under the conditions employed, the alkylation reaction showed typical second-order kinetics, first order with respect to each reactant. The results for the several phenols are summarized in Table I. The rate constants checked within 10%, which is not unreasonable considering the analytical method. The decrease in rate constant with increasing *ortho* substitution in the phenol is consistent with previous observations.[9]

TABLE I

SPECIFIC RATE CONSTANTS FOR THE ALKYLATION OF SEVERAL PHENOLS WITH α-PHENETHYL CHLORIDE AT 50.0°

Phenol	Solvent	k_a (l. mole^{-1} min.$^{-1}$)
Phenol	*p*-Xylene	$3.97 \pm 0.38 \times 10^{-3}$
Phenol	Benzene	$3.66 \pm 0.40 \times 10^{-3}$
Phenol	*p*-Xylene	$1.58 \pm 0.12 \times 10^{-3}$
Phenol	*p*-Xylene	$0.95 \pm 0.11 \times 10^{-3}$ (40°)
p-Cresol	Benzene	$1.69 \pm 0.10 \times 10^{-3}$ (30°)
o-Cresol	Benzene	$0.33 \pm 0.02 \times 10^{-3}$
2,6-Xylenol	Benzene	$1.11 \pm 0.09 \times 10^{-5}$

The kinetic data for the racemization consisted of a series of rotation *vs.* time readings which gave smooth curves when plotted as in Fig. 1. The points shown were determined experimentally, but the smooth curves drawn through them are based on equation 7, which is discussed fully below. Only a fraction of the experimental points are shown, for clarity in the drawing. The evaluation and significance of the rate constants in equation 7 are considered in the following section.

Discussion

The racemization rate data represent loss of optical activity by several paths. Alkylation of the

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(5) H. Hart, W. L. Spliethoff and H. S. Eleuterio, THIS JOURNAL, **76**, 4547 (1954).

(6) R. L. Burwell, Jr., A. D. Shields and H. Hart, *ibid.*, **76**, 908 (1954).

(7) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 687 (1913); E. Downer and J. Kenyon, *ibid.*, 1156 (1939).

(8) H. Hart, THIS JOURNAL, **72**, 2900 (1950).

(9) H. Hart and F. A. Cassis, *ibid.*, **73**, 3179 (1951).

phenol decreases the optical activity of the solutions, because the rotation of the products is very slight. Even when measured on homogeneous product prepared from chloride with a high initial rotation, the rotations amounted to only a few tenths of a degree.[5] The chloride used in the rate studies was only about 20% optically pure, and the products of alkylation were present in low concentrations, so that at most their contribution to the total rotation of the solution would be a few hundredths of a degree, and was neglected[10] in fitting the rate curves. Loss of optical activity can therefore be given by (1)

$$-\frac{d(\mathrm{R^*Cl})}{dt} = k_a(\mathrm{R^*Cl})(\mathrm{PhOH}) + \text{other terms} \quad (1)$$

where (R*Cl) and (PhOH) are the molar concentrations of the optically active α-phenethyl chloride and the particular phenol, respectively. With mesitol alkylation is impossible and the k_a term drops out of the equation.

Since (R*Cl) is proportional to α, the observed rotation, and (PhOH) can be represented by $(a - x)$, where a is the initial phenol concentration and x is its concentration at time t, (1) becomes

$$-\frac{d\alpha}{dt} = k_a(\alpha)(a - x) + \text{other terms} \quad (2)$$

The problem consists of evaluating the "other terms" in (2).

The simplest assumptions for the racemization process are either a first order (in halide) or second order (first order each in halide and phenol) expression, given by

$$-\frac{d\alpha}{dt} = k_a(\alpha)(a - x) + k_r(\alpha) \quad (3)$$

or

$$-\frac{d\alpha}{dt} = (k_a + k_r)(\alpha)(a - x) \quad (4)$$

respectively, where k_r is the racemization specific rate constant. Both of these expressions can be integrated, because x can be evaluated from the second order alkylation data.

$$x = \frac{a^2k_at}{1 + ak_at} \quad (5)$$

Substituting (5) in (3) and integrating, letting $\alpha = \alpha_0$ when $t = 0$, one finds that a plot of $\log (\alpha_0/\alpha)/t$ *vs.* $\log (1 + ak_at)/t$ should be linear with a slope of +1.00 and an intercept of k_r. Such plots were indeed linear for all the runs, but their slopes were negative. This eliminates equation 3.

A similar integration of (4) requires that a plot of $\log \alpha_0/\alpha$ *vs.* $\log (1 + ak_at)$ be linear and pass through the origin. Such plots did pass through the origin and approached linearity near the beginning of a run, but showed a distinct and consistent upward curvature from linearity as the run progressed (see Fig. 2). The direction of curvature suggests that racemization was more extensive than this mechanism predicts. Presumably products of the alkylation reaction (alkylated phenol, hydrogen chloride, or both) caused additional racemization of the α-phenethyl chloride.[11]

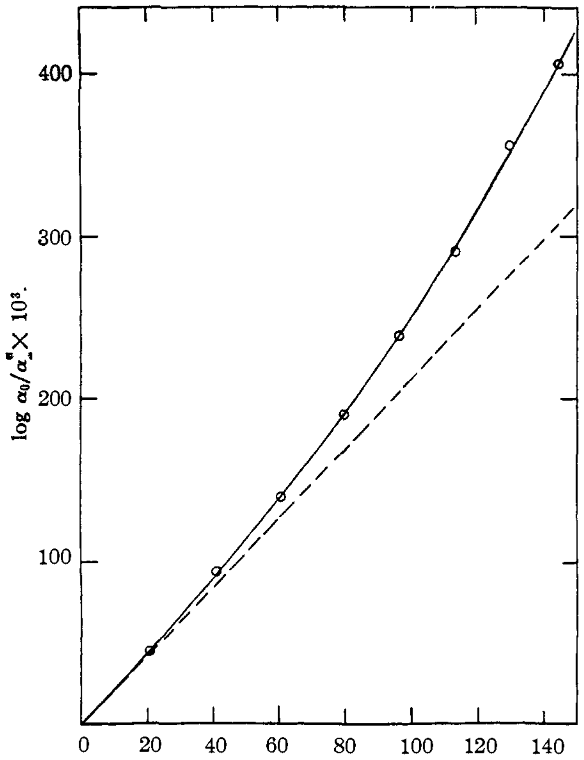

Fig. 2.—Lack of fit of equation 4 shows the need for additional terms. Data are for α-phenethyl chloride in phenol at 50°.

Equation 4 was therefore expanded to include terms which represent racemization due to the alkylation products. This is easily done, for the concentration of alkylated phenol is x and that of hydrogen chloride is proportional to x, assuming Henry's law to hold. We then obtain

$$-\frac{d\alpha}{dt} = (k_a + k_r)(\alpha)(a - x) + (k_{\mathrm{AP}} + k_{\mathrm{HCl}})(\alpha)(x) \quad (6)$$

where k_{AP} is the specific second-order rate constant for racemization due to alkylated phenol (analogous to k_r for the initial phenol) and k_{HCl} is a combination of the rate constant for hydrogen chloride-catalyzed racemization and the Henry's law constant for solubility of hydrogen chloride in the medium.[12] Equation 6 integrates to (7).

$$\frac{\log \alpha_0/\alpha}{t} = \frac{k_a + k_r - k_{\mathrm{AP}} - k_{\mathrm{HCl}}}{k_a}\,\frac{\log(1 + ak_at)}{t} + a(k_{\mathrm{AP}} + k_{\mathrm{HCl}}) \quad (7)$$

From the intercept of the linear plots of $\log (\alpha_0/\alpha)/t$ *vs.* $\log (1 + ak_at)/t$ one can evaluate the sum $(k_{\mathrm{AP}} + k_{\mathrm{HCl}})$, called k_x, and knowing k_a, one can evaluate k_r from the slope. The values of these constants are given in Table II.

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[10] Near the beginning of a run, when alkylated phenol might have an appreciable rotation, its concentration would be very low. Later on in a run, alkylated phenol is formed principally from racemic chloride, and therefore cannot contribute to the over-all rotation. We feel this justifies the conclusion that contributions from the alkylated phenol will be negligible.

[11] It is hardly likely that this lack of fit is due to a medium effect, even though the solutions are admittedly quite concentrated for kinetic studies. Since increased substitution in a phenol decreases its ability to racemize α-phenethyl chloride, a simple medium effect would predict the opposite curvature from that which was observed.

[12] It is not *a priori* necessary that the last term in equation 6 contain two constants, but evidence will be presented below favoring racemization by both of these paths.

TABLE II

SPECIFIC RATE CONSTANTS FOR THE RACEMIZATION OF α-PHENETHYL CHLORIDE IN SEVERAL PHENOLS AND *p*-XYLENE AT 50.0°

Phenol	k_r[a], l. mole^{-1} min.$^{-1}$	k_x,[a] l. mole^{-1} min.$^{-1}$
Phenol	$4.0 \pm 0.3 \times 10^{-3}$	$14.75 \pm 0.2 \times 10^{-3}$
Phenol (40.0°)	2.5×10^{-3}	6.9×10^{-3}
Phenol (30.0°)	0.9×10^{-3}	4.9×10^{-3}
p-Cresol	$3.1 \pm 0.2 \times 10^{-3}$	$11.0 \pm 1.0 \times 10^{-3}$
o-Cresol	$0.97 \pm 0.02 \times 10^{-3}$	$3.1 \pm 0.1 \times 10^{-3}$
2,6-Xylenol	1.96×10^{-5}	
Mesitol	$1.92 \pm 0.15 \times 10^{-5}$	

[a] Where estimates of error are given, the *k* is a mean value from several runs. Other constants are for single runs.

With mesitol, where no alkylation was possible, and with 2,6-xylenol, where alkylation was exceedingly slow (see Table I), the k_a, k_{AP} and k_{HCl} terms in (6) could be neglected, giving

$$-\frac{d\alpha}{dt} = k_r(\alpha)(a) \qquad (8)$$

Linear plots through the origin were obtained in plotting log α_0/α *vs.* *t*, from which k_r was evaluated.

Fit of equation 7 to the experimental data is shown in Fig. 1, where the smooth curves are drawn using the constants in Table II, and the dots represent experimental points.[13]

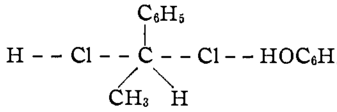
From the data of Tables I and II one obtains, in the usual manner, an activation energy of about 15 kcal./mole and an activation entropy of about −25 cal./° for both the alkylation and racemization reactions involving phenol (k_a and k_r).

Interpretation

First, we wish to justify the treatment of k_x as a sum of two separate rate constants; that is, to demonstrate that a hydrogen chloride term is necessary in the rate equation. It is not necessary to justify a term for the alkylated phenol (k_{AP}), for certainly, if the original phenols cause α-phenethyl chloride to racemize, then so too must their alkylation products.

Substitution in a phenol causes a decrease in k_r, particularly when substitution is *ortho* to the hydroxyl. This drop is particularly sharp for the second *ortho* substituent (compare phenol, *o*-cresol and 2,6-xylenol, Table II). One would therefore expect that the alkylation product in any given case should be less efficient at racemizing α-phenethyl chloride than the original phenol (*i.e.*, $k_{AP} < k_r$). If k_x represented only k_{AP} (and not k_{HCl}) then it should be smaller than k_r. Table II shows that this is not the case; wherever data are available, k_x is larger than k_r. This means that an additional racemization path, also proportional to the product $(\alpha)(x)$ must be involved. Presumably this path involves hydrogen chloride, the other alkylation product.

But when anhydrous hydrogen chloride was passed through a dry benzene solution of α-phenethyl chloride at 50° for one hour, very little racemization occurred. The hydrogen chloride must therefore function in conjunction with phenol molecules, possibly according to a scheme such as



$$\mathrm{H - - Cl - - \overset{C_6H_5}{\underset{CH_3\ \ H}{C}} - - Cl - - HOC_6H_5}$$

Since the total concentration of hydroxylic species remains constant throughout a run, second, rather than third-order kinetics are observed for the k_{HCl} term.[14]

The near identity of the rate constants for alkylation and racemization (compare k_a, Table I, with k_r, Table II) can hardly escape notice. Furthermore, the pattern of change in these constants with changing phenol structure is so similar that one is tempted to assume a common rate-determining step for both processes. Presumably, this would be the ionization of α-phenethyl chloride, facilitated by the hydroxylic solvent. It has already been established[15] that the free hydroxyl group is necessary for the uncatalyzed alkylation reaction, and this also appears to be the case for the racemization; substitution ortho to the hydroxyl decreases the ionizing power of the phenols. The similar temperature coefficients of the rate constants for alkylation and racemization are also consistent with this interpretation.

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[13] Several other plausible mechanisms were tested and found to be untenable. For a discussion, see W. L. Spliethoff, Doctoral Dissertation, Michigan State College, 1953.

[14] Presumably hydrogen chloride is more polar in phenol than in the anhydrous state, due to interaction with the hydroxyl group. This interaction has been omitted from the schematic representation.

[15] H. Hart, F. A. Cassis and J. J. Bordeaux, THIS JOURNAL, **76**, 1639 (1954).