Kinetic Studies on Solvolysis. VIII. Phenolysis of Optically Active α-Phenethyl Chloride in Phenol-Benzene Solvent—Three-stage Mechanism in the S_N1-Type Solvolysis*

By Kunio OKAMOTO, Ken-ichi TAKEUCHI and Haruo SHINGU

(Received June 23, 1961)

The mechanism of phenolysis of α-phenethyl chloride has been extensively investigated by Hart and his co-workers[1]. These authors[1b] carried out the phenolysis in the absence of basic substances and noted that the near identity of rate constants for the racemization of α-phenethyl chloride and for the nuclear alkylation of phenol in various mixtures of phenols and aromatic hydrocarbons. Although they suggested that a common rate-determining step for both reactions would be the ionization step of the halide, they did not refer to the solvolytic

---

* Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961. Part VII. of this series: K. Okamoto, K. Takeuchi and H. Shingu, This Bulletin, 34, 1137 (1961).

[1] a) H. Hart, W. L. Spliethoff and H. S. Eleuterio, *J. Am. Chem. Soc.*, 76, 4547 (1954); b) H. Hart and W. L. Spliethoff, ibid., 77, 833 (1955).

nature of the reaction and presented a second-order rate equation with some additional terms for explaining the rate data. In Part V of this series²⁾ we have illustrated how a reliable criterion of the S_N1 (first-order) two-step mechanism may be established for the phenolysis of *tert*-butyl halides by examination of the rate dependence on initial concentrations of the added base and also on solvent compositions. In addition, we have suggested the applicability of the first-order mechanism to the aralkyl system. Some doubt, therefore, arises about the validity of the second-order mechanism suggested by Hart¹ᵇ⁾ for this phenolysis.

One of the purposes of this study was to re-investigate the previous work¹ᵇ⁾ in the presence of a base, especially at lower initial concentrations of the chloride, and to substantiate the applicability of S_N1 mechanism on the phenolysis of α-phenethyl system.

Another purpose was to clarify the details of kinetic nature of the intermediates of this phenolysis, and to examine the concept of Winstein's ion-pair intermediates³⁾.

First-order Nature of the Polarimetric and Titrimetric Rate Constants.—We have previously²⁾ shown that the titrimetric rate of the phenolysis of α-phenethyl chloride obeys good first-order kinetics in a phenol-nitrobenzene mixture both in the presence of and in the absence of sodium phenolate. In this study anilinium phenolate was used as a base, because in the phenolysis with sodium phenolate crystalline precipitate of sodium chloride makes the polarimetric measurement impossible.

The polarimetric rate constants, k_α, were measured in phenol-benzene (1 : 1 by weight) at 25°C, and satisfactory first-order behavior was observed in the decrease of optical activity, irrespective of presence or absence of the added base, this being illustrated graphically in Fig. 1. The observed rate constants are summarized in Table I.

Titrimetric rate constants, k_t, were also measured for comparison with the corresponding polarimetric values. Decrease of anilinium phenolate or increase of hydrogen chloride associated with the phenolysis obeyed good first-order kinetics, this being illustrated graphically in Fig. 2. The observed titrimetric rate constants are summarized also in Table I.

From these results it is clear, as previously anticipated²⁾, that the S_N1-type solvolytic mechanism is the only reasonable one for the phenolysis, at least in the range of lower concentrations of the chloride.

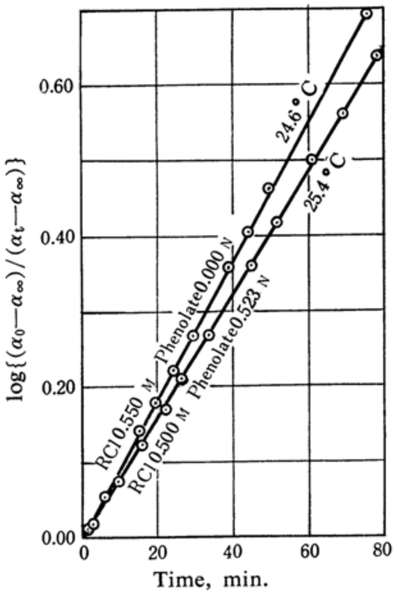

Fig. 1. Polarimetric rate of phenolysis at 25°C of (−)-α-phenethyl chloride in 50 wt.% phenol-benzene.

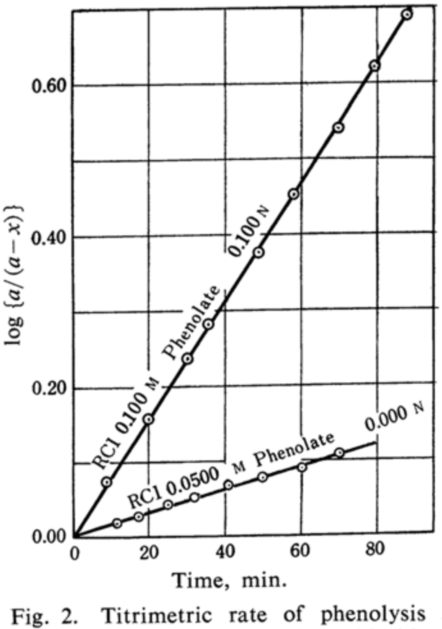

Fig. 2. Titrimetric rate of phenolysis at 25.0±0.1°C of α-phenethyl chloride in 50 wt.% phenol-benzene.

Relationships between the Rate Constants and the Initial Concentrations of the Added Base.—As illustrated graphically in Fig. 3, in the range of the initial anilinium phenolate concentrations from 0 to 0.5 M, the titrimetric rate constant rises very steeply with the phenolate concentration, reaches a maximum value and then decreases gradually. On the other hand,

---

2) H. Shingu and K. Okamoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 111 (1960).

3) S. Winstein, A. H. Fainberg and G. C. Robinson, *Chem. & Ind.*, **1954**, 664.

TABLE I. SUMMARY OF TITRIMETRIC AND POLARIMETRIC RATE CONSTANTS FOR THE PHENOLYSIS OF α-PHENETHYL CHLORIDE IN 50 WT. % PHENOL-BENZENE AT 25.0±0.1°C.

RCl M	Anilinium phenolate N	Me_4NCl N	Method	Initial $\alpha°$	Final $\alpha°$	10^2k_1 min^{-1}	Conversion %
0.0500			Tit.			0.357	27
0.0500	0.0049		Tit.			1.38	5.8
0.0500	0.0095		Tit.			1.69	13.6
0.0500	0.0200		Tit.			1.81	33.6
0.0500	0.0500		Tit.			1.82	81.5
0.100			Tit.			0.411	26.0
0.100	0.0402		Tit.			1.82	38.2
0.100	0.100		Tit.			1.76	79.5
0.100	0.104		Tit.			1.84	77.5
0.100	0.265		Tit.			1.70	73.6
0.550			Pol.[a]	−4.84	0.00[a]	2.09	100
0.550	0.470		Pol.[b]	−4.77	+0.89[b]	1.92	100
0.500	0.523		Pol.[c]	−4.18	+1.20[c]	1.92	100
0.495	0.513		Pol.[d]	−4.51	+1.24[d]	1.87	100
0.400	0.513		Pol.[e]	+1.57	−0.47[e]	1.96	100
0.100		0.107	Tit.			0.640	40.5
0.100	0.107	0.107	Tit.			2.26	85.0
0.100	0.109	0.107	Tit.			2.26	81.3
0.100	0.109	0.054	Tit.			2.14	79.8

a 24.6°C, b 25.4°C, c 25.4°C, d 25.3°C, e 25.2°C
a—e Errors of reading of rotations, ±0.02∼0.03°

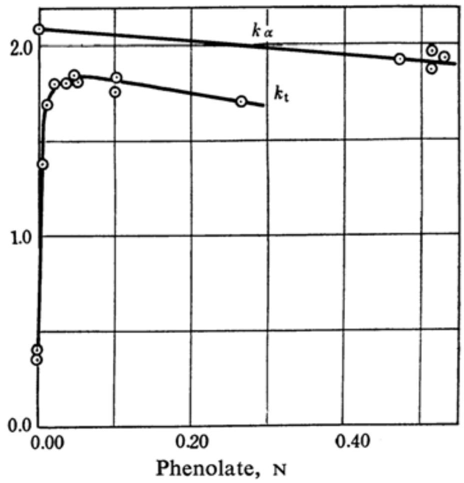

Fig. 3. Effect of initial concentration of anilinium phenolate on phenolysis of α-phenethyl chloride in 50 wt.% phenol-benzene at 25°C.

the polarimetric rate constants exceed the titrimetric values in the whole investigated range of the initial concentrations of the phenolate. The discrepancy between k_α and k_t seems to be definite even in the higher phenolate concentrations. The k_α's may be regarded as fairly constant, because the minor decrease with phenolate concentrations would be explained as originating from the decrease of the net phenol concentration due to the added base.

This result, i. e., the existence of constant gap between k_α and k_t, appears to be similar to the one which Winstein and Robinson(4) found for acetolysis of *threo*-3-*p*-anisyl-2-butyl system. These authors(4) claimed their results as the experimental bases of their "ion-pair" multi-step mechanism. However, the following results of product analysis and of analysis of the steric course for this phenolysis enforced us to consider about the other type of intermediates and mechanism.

Product Analysis and Steric Course of the Phenolysis.—When the reactions were carried out in the presence of anilinium phenolate, it was found that the isolated products were α-phenethyl phenyl ether and a minor amount of α-phenethylphenols. On the other hand, as previously found by Hart and his coworkers(1a), in the absence of the phenolate the only reaction product at a comparable reaction time was a minor amount of α-phenethylphenols. Furthermore, the hydrogen chloride cleavage of α-phenethyl phenyl ether into α-phenethyl chloride and phenol was quite rapid (half-life time, 1∼2 min.) in comparison with the phenolysis. In view of these analytical results and the rate-relation, it is clear that the consumption of hydrogen chloride by the anilinium phenolate eliminates the reverse

---

4) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

formation of α-phenethyl chloride, whereas in the absence of the phenolate the rapid reverse reaction interrupts formation of the phenyl ether.

The establishment of the steric course for this phenolysis made the mechanistic situation clearer. When optically active α-phenethyl chloride was phenolyzed in the absence of anilinium phenolate, the polarimetric measurement showed that almost completely racemic α-phenethylphenols were produced, this being shown in Table I. However, in the presence of anilinium phenolate partially optically active α-phenethyl phenyl ether with retained configuration was obtained along with a minor amount of almost (more than 99%) racemic α-phenethylphenols. It is evident that these optically active products should be derived from an optically active intermediate. This rules out the Winstein's "ion-pair" mechanism[3] which postulates racemic intermediates.

Absence of the Common-ion Effect. — As mentioned above the titrimetric rate constants showed good first-order behavior. This indicates that there is no rate suppression by anilinium hydrochloride produced during the reaction. Furthermore, for the reaction carried out in the presence of tetramethylammonium chloride (0.05~0.100 N) the titrimetric rate constants showed also good first-order kinetics and their values were a little higher than those in the absence of the chloride, probably owing to some ionic strength effects (cf. Table I). These results indicate that there is no common-ion depression for the phenolysis rate of α-phenethyl chloride.

In the case of phenolysis for *tert*-butyl chloride[2], it was found that tetramethylammonium chloride showed extraordinarily marked common-ion depression, and it was concluded that the ion-pair intermediate reacted with the chloride ion, giving the starting chloride through exchange of chloride ion of the intermediate. On the basis of this mechanism the absence of common-ion effect in α-phenethyl system may be explained by the relatively large stability of the ion-pair intermediate. This stability is reflected in the solvolysis rate in α-phenethyl system and may be the cause of the existence of two kinds of intermediates for this system.

Thus it may be concluded that the ion-pair intermediate in this case has no exchangeability for the chloride ion because of the more dipole-like nature of the ion-pair associate or the tightness of the solvation shell around the ion-pair.

Mechanism of the Phenolysis of α-Phenethyl Chloride. — In general the existence of the discrepancy between k_α and k_t merely indicates that the racemization (or ionization) process should preceed the product-formation stage. However, if the discrepancy vanishes at higher concentrations of the base or, in other words, if the rate of product-formation becomes equal to that of racemization (or ionization), it indicates that both of the processes should be connected with the same intermediate and the reaction should obey the two-stage mechanism. This can easily be illustrated by total rate expression for the common S_N1-type two-stage mechanism. A pertinent example for this is found in the comparison of the ionization rate constants and product-formation rate constants for the acetolysis in 2-*p*-anisylpropyl system[5], although the authors[5] postulated a three-stage mechanism with two species of the intermediate, i. e., "intimate" and "solvent separated" ion-pair.

On the other hand, if the increase of the base concentration dose not lessen the gap between k_α and k_t even at the higher concentrations and the preponderance of k_α over k_t is definitely observed, any rate expression derived from the two-stage mechanism would fail to explain this gap. Therefore, it is suggested that there should be certain, i. e., kinetically distinct, process intervening between the racemization and the product-formation process; in other words, two species of intermediates would be required between these processes, at least. These inferences, of course, are drawn irrespective of the structures of the intermediates and also irrespective of the details of the mechanism for each stage.

From these considerations we are led to postulate the following three-stage (two-intermediate) mechanism for the phenolysis of α-phenethyl chloride. Since the intermediates involved in this reaction should have optical activities, it is required to divide the three-stage mechanism into two parallel series of three-stage reactions of the optically antipodal chlorides, (+)-RCl and (−)-RCl. Thus, each of the series of the reactions involves two species of antipodal intermediates, I_1 and I_2, and the racemization must take place by way of an equilibration between the first antipodal intermediates, i. e., (+)-I_1 and (−)-I_1. If the racemization is caused by an equilibration between the second antipodal intermediates, the coincidence of k_α and k_t at higher phenolate concentrations would result; the process could then be represented by a two-stage mechanism and the kinetical discrimination of I_1 and I_2 would be impossible. The postulated mechanism is illustrated in the following kinetic scheme.

---

[5] S. Winstein and A. H. Fainberg, ibid., **80**, 459 (1958).

$$\begin{tikzcd}
(+)\text{-RCl} \arrow[r, shift left, "k_1"] & (+)\text{-I}_1 \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[d, shift right, "k_4"'] & (+)\text{-I}_2 \arrow[l, shift left, "k_{-2}"] \arrow[r, "k_3"] & (+)\text{-RY} \\
(-)\text{-RCl} \arrow[r, shift left, "k_1"] & (-)\text{-I}_1 \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[u, shift right, "k_4"'] & (-)\text{-I}_2 \arrow[l, shift left, "k_{-2}"] \arrow[r, "k_3"] & (-)\text{-RY}
\end{tikzcd}$$

In this scheme k_3 represents the ove-all rate constant for the product formation stage and actually means the sum of two terms, namely, the rate constant, k_3', for the solvent phenol molecule (YH) and the rate constant, $k_3'' \times [\text{Y}]$, for the phenolate (Y).

Using steady-state conditions for the concentrations of these intermediates, we obtain the rate expressions for k_α and k_t in Eqs. 1 and 2, respectively.

$$k_\alpha = \frac{k_1}{1+\dfrac{k_{-1}}{2k_4+\{k_2k_3/(k_3+k_{-2})\}}} \tag{1}$$

$$k_t = \frac{k_1}{1+\dfrac{k_{-1}}{k_2k_3/(k_3+k_{-2})}} \tag{2}$$

Since the first intermediate, I_1, is considered as an ion-pair (see the next section), k_1 represents an ionization rate constant. Thus it is clear from Eq. 1 that the observed racemization rate constant, k_α, is not always equal to the ionization rate constant, k_1, except at a limiting condition, $k_4 \gg k_{-1}$. This condition is, of course, unapplicable to this reaction.

From Eq. 1, the independency of k_α on the initial concentration of the phenolate is explained by the limiting condition, $k_4 \gg k_2$, this being shown in Eq. 3.

$$k_\alpha = k_1/\{1+(k_{-1}/2k_4)\} \tag{3}$$

The constancy of k_t as the first-order rate constant is also explained by the limiting condition, $k_3 \gg k_{-2}$, this being shown in Eq. 4.

$$k_t = k_1/\{1+(k_{-1}/k_2)\} \tag{4}$$

Thus the constant gap between k_α and k_t observed for higher phenolate concentrations can be explained by comparing the above two equations, 3 and 4.

With diminution of the phenolate concentrations, however, the value of k_3 decreases, and reaches finally, in the absence of the phenolate, the value of k_3', i.e., the rate constant for the solvent phenol. This explains a sudden decrease of k_t in the vicinity of zero-concentration of the phenolate (cf. Fig. 3).

Discussion on the Structures of the Intermediates.— In consideration of the existence of the equilibration between the antipodes $(-)$-I_1 and $(+)$ -I_1 and of the lack of common-ion depression, the intermediate I_1 may be assumed to be an ion-pair surrounded by a solvation shell, and in the shell the carbonium cation may rotate or invert over a difintie but small potential barrier with a relatively large rate constant k_4, giving another antipodal intermediate, I_1. From the predominant retention of configuration in the product, the second intermediate I_2 may be assumed to be a kind of quadrupolar associate consisting of an α-phenethyl chloride ion-pair and a molecule of phenol or of anilinium phenolate originated from one of the members of the solvation shell. At the third stage, i. e., product-formation step, these quadrupoles may collapse to the products with mostly retained configuration. This stage may proceed similarly to the intramolecular reaction of $\text{S}_\text{N}i$-type⁽6⁾.

As to structure of the intermediates, a short comment about Winstein's "intimate" and "solvent separated" ion-pair mechanism⁽3⁾ seems to deserve mention here. It has already been stated that Winstein's three-stage mechanism was not necessary for explaining the acetolysis in 2-*p*-anisyl-1-propyl system⁽5⁾ but that the common two-stage mechanism was applicable to this system. In contrast to 2-*p*-anisyl-1-propyl system, however, for the *threo*-3-*p*-anisyl-2-butyl system⁽4⁾ Winstein and Robinson found that the gap between the k_α line and the k_t line in acetolysis actually widened as the concentration of the added lithium perchlorate increased. It is evident from our conclusion in the previous section that the definite discrepancy between k_α and k_t for this system requires two discrete intermediates in the formulation of mechanism. In regard to the structures of the intermediates, however, Winstein's two kinds of ion-pairs, namely "intimate" and "solvent separated", do not seem to be kinetically distinguishable as discrete intermediates, because such ion-pairs should be quite rapidly interchanged among them and their stabilities would be closely the same. Therefore, Winstein's discrimination between the ion-pair structures does not seem chemically well founded, and is inapplicable not only to this system but also to any other system which requires two kinds of intermediates.

For the first intermediate in this *threo*-3-*p*-anisyl-2-butyl system an internally compensated phenonium ion-pair structure, just as postulated by Winstein and Robinson⁽4⁾, may be regarded as kinetically stable and discrete. The second intermediate which should also be a stable species, would be formulated as chemically different from the first one. In analogy with the second intermediate in the phenolysis of α-phenethyl chloride, it seems reasonable to postulate some stable species, such as a new

---

6) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, **1937**, 1252.

phenonium ion-pair involving an acetate ion instead of the arylsulfonate ion involved in the first intermediate, or a quadrupolar associate between the first phenonium ion-pair and a molecule of acetic acid.

Unlike in the phenolysis of active α-phenthyl chloride, the racemization rate in the acetolysis for this system is equalized to the ionization rate owing to the formation of internally compensated phenonium ion-pair. This is interpreted by the kinetic Eq. 1 presented for the polarimetric rate constant of the phenolysis, because, in such a specific case where the interconversion rate between the first antipodal intermediates, k_4, is quite rapid, the equation becomes

$$k_\alpha = k_1 \qquad (5)$$

In addition, the discrepancy between k_α and k_t for this system may also be accounted for by application of Eq. 4. Thus, it is clear that the kinetic characteristics of this *threo*-3-*p*-anisyl-2-butyl system are interpreted by the same mechanism as presented for the phenolysis of α-phenetyl chloride.

Experimental[7]

Materials.—The preparation of racemic and of optically active α-phenethyl chloride followed previous practice[8]; b. p. 68.0°C/16 mmHg. for racemic chloride; b. p. 55.0°C/11 mmHg., $[\alpha]^{24.4}_{\mathrm{D}}+17.76\pm 0.03°$, l 1 dm., homogeneous, and b. p. 59.0°C/12 mmHg, $[\alpha]^{31}_{\mathrm{D}}$ $-36.5°$, l 1 dm., homogeneous. Aniline, phenol and benzene (reagent grade for each) were dried and purified by fractional distillation; b. p. 42.0~43.0°C/1 mmHg, 179.0~181.0°C and 80.0 ~81.0°C, respectively. Reagent grade tetramethylammonium chloride was dried to constant weight in a tarred flask at 120~130°C in vacuo.

Kinetic Measurements. — The phenolyses were carried out by the usual method[8], the diminution of anilinium phenolate (or the development of hydrogen chloride) being followed by titration of aliquots (1.000 cc.) with standard perchloric acid (or sodium acetate) in acetic acid. Each run was followed to 60~70% completion.

For the polarimetric rate measurements with Zeiss-Winckel "Kreispolarimeter 0.01°", the reaction mixtures, prepared at the reaction temperature, were immediately placed into a jacketed 2 dm. polarimeter tube maintained at the reaction temperature by circulation of water from a constant temperature bath.

Phenolyses of Racemic and Optically Active α-Phenethyl Chloride in 50 wt.% Phenol-Benzene in the Presence of Anilinium Phenolate.—A solution of ($\pm$)-α-phenethyl chloride (5.02 g.) in 0.52 N anilinium phenolate (70 cc.), prepared from desired weights of aniline and 50 wt.% phenol-benzene at 25.0°C, was kept at 25.0°C for 4 hr. (ca. six half-lives). The phenolysis mixture was then washed twice with 30 cc. portions of water and extracted with four 50 cc. portions of 10% aqueous sodium hydroxide and three 30 cc. portions of 20% aqueous sodium hydroxide. After acidification of the alkaline extract, the liberated phenols were extracted with benzene. The benzene solution was dried, and after distillation of the benzene vacuum distillation of the residual material gave phenol (16.8 g., b. p. 69.0°C/7 mmHg) and mixture of *o*- and *p*-α-phenethylphenols (0.50 g., b. p. 140~155°C/3 mmHg; lit.[1a] 165~180°C/5~6 mmHg). After the alkaline extraction of the phenolysis mixture the remaining benzene layer was washed with water and dried with anhydrous sodium sulfate. Distillation of the benzene afforded an oily material which was distilled in vacuo to give α-phenethyl phenyl ether (4.5 g., b. p. 123~128°C/4 mmHg, m. p. 35.0~36.0°C; lit.[9] 143 ~145°C/10 mmHg, m. p. 38~39°C) and a mixture of *o*- and *p*-α-phenethylphenols (0.50 g., b. p. 140~145°C/5 mmHg). No attempt was made to determine the ortho-para ratio of the phenol mixture. There was not found any styrene fraction before the α-phenethyl phenyl ether fraction, and the recovered benzene did not give any styrene peak in gas-liquid partition chromatographical analysis.

The phenolysis of ($-$)-α-phenethyl chloride (α_{D}, see materials section) was carried out polarimetrically and then the product analysis of the reaction mixture was made. A solution of ($-$)-α-phenethyl chloride (5.220 g.) in 0.550 N anilinium phenolate (70.0 cc.) was kept at 25.0°C for 22 hr. (ca. 44 half-lives). Part of the solution was used for the polarimetric run at 25°C. The combined reaction mixtures, similarly treated to the run with the racemic chloride, gave (+)-α-phenethyl phenyl ether (4.16 g., b. p, 111.0~113.0°C/2 mmHg, yield 56.5%, $[\alpha]^{34}_{\mathrm{D}}+2.29°$, l 1 dm., homogeneous; Found: C, 84.68; H, 7.14. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12%) and ($-$)-α-phenethylphenols (a mixture of *o*- and *p*-derivatives, b. p. 150~165°C/7 mmHg, yield 13.6%, $[\alpha]^{34}_{\mathrm{D}}-0.42°$, l 1 dm., c 23.8, benzene).

The second run carried out under the same conditions with (+)-α-phenethyl chloride (3.525 g., α_{D} see materials section) solution (50.0 cc.) of 0.552 N anilinium phenolate afforded 3.0 g. of ($-$)-α-phenethyl phenyl ether (b. p. 133~135°C/5 mmHg, n^{25}_{D} 1.5665, yield 60.0%, $\alpha^{24.7}_{\mathrm{D}}+1.21°$, l 1 dm., homogeneous; Found: C, 84.93; H, 7.20%).

Phenolysis of ($\pm$)-α-Phenethyl Chloride in 50 wt.% Phenol-Benzene in the Absence of Anilinium Phenolate.—A solution of ($\pm$)-α-phenethyl chloride (4.92 g.) in 50 wt.% phenol-benzene (62.8 g.) was kept at 20~25°C for 22 hr., and then at 50.0°C for 7 hr. After similar treatment to the run in the presence of anilinium phenolate, the benzene layer after alkaline extraction gave 0.10 g. of α-phenethylphenols (b. p. 132~133°C/2 mmHg) and from the alkaline extract 3.5 g. of α-phenethylphenols (140~156°C/4 mmHg) was isolated.

Hydrogen Chloride Cleavage of α-Phenethyl Phenyl Ether in 50 wt.% Phenol-Benzene.—The cleavage was followed titrimetrically. In a 20 cc.

---

[7] Microanalyses by Microanalytical Center, Kyoto University.

[8] K. Okamoto, K. Takeuchi and H. Shingu, This Bulletin, 34, 1132 (1961).

[9] H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 519 (1954).

volumetric flask, α-phenethyl phenyl ether (137 mg.) solution of 0.045 N hydrogen chloride was made at 25°C. The reaction percentage was estimated to be 74.0% at two minutes after mixing. The diminution of hydrogen chloride reached a minimum value (84.7% of conversion for ether), then the gradual increase of hydrogen chloride concentration, due to the slow phenolysis of α-phenethyl chloride produced, was observed.

Summary

1. Titrimetric and polarimetric rate constants (k_t and k_α) for phenolysis of α-phenethyl chloride in 50 wt.% phenol-benzene at 25°C were measured, and satisfactory first-order behavior was observed irrespective of presence or absence of anilinium phenolate. From this the S_N1-characteristics of this phenolysis was concluded.

2. The values of k_α's were fairly constant at any phenolate concentrations (0.0∼0.6 N). The k_t's were also fairly constant at higher phenolate concentrations. However, the k_t's gave smaller values than the k_α's, and showed a sudden decrease in the vicinity of zero phenolate concentration. The gap between the k_α line and k_t line was not diminished and remained fairly constant as the phenolate concentration increased.

3. In the presence of anilinium phenolate the main product was α-phenethyl phenyl ether with predominantly retained configuration, whereas in the absence of the phenolate only a minor amount of α-phenethylphenol was obtained.

4. From the constant gap observed between k_α and k_t it was generally concluded that the phenolysis should proceed by way of a two-intermediate (I_1 and I_2) three-stage mechanism. In view of the predominant retention of configuration in the product, it was postulated that the intermediates should be optically active. Hence the mechanism was divided into parallel series of the three-stage processes for the optically antipodal chlorides and intermediates, namely,

$$(+)\mathrm{RCl} \rightleftarrows (+)\mathrm{I}_1 \rightleftarrows (+)\mathrm{I}_2 \rightarrow (+)\mathrm{RY}$$

and $$(-)\mathrm{RCl} \rightleftarrows (-)\mathrm{I}_1 \rightleftarrows (-)\mathrm{I}_2 \rightarrow (-)\mathrm{RY}$$

These parallel series of the processes were connected with each other by fairly rapid equilibration between the first antipodal intermediates ($-I_1$ and $+I_1$). For the first intermediate was suggested an ion-pair surrounded by a solvation shell and for the second a kind of quadrupolar associates which consist of the ion-pair and the reactant dipole (phenol or anilinium phenolate).

5. It was pointed out that a necessary condition for the existence of three-stage mechanism is a kinetically-definite stabilization of the two kinds of intermediates. This stabilization was verified by the absence of common-ion depression for this phenolysis rate. It was also pointed out that unstable ion-pair intermediates, like "solvent separated" and "intimate" ion-pair, could not be kinetically distinguished among themselves, and that in this case any three-stage formulation actually converged to two-stage treatment. This was shown in the case of acetolysis in 2-*p*-anisylpropyl system to which Winstein and Fainberg[5] assumed their three-stage mechanism to be applicable.

6. It was shown that Winstein's three-stage mechanism with the "intimate" and "solvent separated" ion-pairs is generally unapplicable to any cases where a three-stage is required, e. g., not only to this phenolysis but also to the acetolysis in *threo*-2-*p*-anisyl-3-butyl system[4]. For the latter a three-stage mechanism similar to the one suggested for this phenolysis in α-phenethyl system was presented. Fairly stable, two discrete intermediates, namely, a phenonium ion-pair for the first intermediate and a quadrupolar associate between the first intermediate and acetic acid molecule for the second were suggested.

Department of Fuel Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto