lated yield of pure norbornane was 132 mg (71%): nmr ($CDCl_3$) δ 2.10 (m, 2, $\geqslant$CH), 1.30–1.76 (m, 3.6, exo >CHH), 1.26 (m, 1, HC-*tert*-Bu), 0.98–1.18 (m, 2.4, endo >CHH), 0.92 (s, 9, $(CH_3)_3C$]. Deuterium addition had occurred 80% endo,cis.

Diimide Reduction.—The reduction of 200 mg (1.35 mmol) of *syn*-7-*tert*-butylnorbornene with diimide was attempted as described above. The olefin was exposed to a fourfold molar excess of diimide generated by two charges of potassium azodicarboxylate over a period of 3 hr. Analysis by vpc (300 ft × 0.01 in. DC-550 silicone column, 115°, 30 psig) showed that the starting olefin was recovered quantitatively.

Silver Nitrate Complexation.—*syn*-7-*tert*-Butylnorbornene failed to complex silver nitrate in aqueous solution. The olefin showed identical retention times on both silver nitrate–ethylene glycol and ethylene glycol vpc columns.

Oxymercuration.—Oxymercuration of the syn olefin was attempted with mercury(II) acetate in aqueous tetrahydrofuran.[27] The reaction was stirred at room temperature for 24 hr; no discharge of the characteristic yellow color of the mercury salt suspension occurred. The reaction was worked up according to the standard procedure to recover unreacted olefin. The absence of product was confirmed by vpc analysis.

Addition of Thiophenol.—A solution of 110 mg (1.0 mmol) of thiophenol and 150 mg (0.84 mmol) of *syn*-7-*tert*-butylnorbornene (84% syn olefin, 16% 7-*tert*-butylnorbornane) in 1 ml of *n*-hexane was stirred at 0° under nitrogen. The solution was irradiated with a Hanovia 100-W quartz ultraviolet lamp. Samples were removed periodically through a rubber septum and were analyzed by vpc for the disappearance of *syn*-7-*tert*-butylnorbornene; 7-*tert*-butylnorbornane was utilized as an internal standard. After 3.5 hr of irradiation the concentration of syn olefin was unchanged. The irradiation was interrupted, and 950 mg (1.0 mmol) of norbornene was injected into the reaction. Irradiation of the reaction mixture was resumed, and after 25 min 75% of the norbornene had reacted; after 50 min only 5% of the norbornene remained. No change in the concentration of the *syn*-7-*tert*-butyl compound was apparent.

Registry No.—**1**, 32640-84-9; **2**, 32640-83-8; **9**, 33905-54-3; **9** anti isomer, 33905-55-4.

Kinetic α-Deuterium Isotope Effects in the Reactions of Benzyl Chlorides with Cyanide Ion and in the Solvolyses of Benzyl Chlorides[1]

Alfred V. Willi,*[2] Chih-kuo Ho, and Alireza Ghanbarpour

College of Pharmaceutical Sciences, Columbia University, New York, New York 10023

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α-Deuterium isotope effects have been determined for the reactions with cyanide ion and the solvolyses of *m*-chlorobenzyl chloride, benzyl chloride, and *p*-methylbenzyl chloride in 55% (by vol) aqueous Methyl Cellosolve. In almost all experiments solvolysis occurs parallel to reaction with CN^-, and it is necessary to apply eq 3 for the calculation of k_2 for the reaction with CN^-. Values of k_1 have been evaluated separately in experiments without CN^- at the same ionic strength. Only the reaction with CN^- and the solvolysis of *m*-chlorobenzyl chloride are examples of practically pure SN2 processes, and the isotope effects are nearly equal to unity. The unusually high result of k_H/k_D = 1.25–1.31 (50°) in the reaction of *p*-methylbenzyl chloride with cyanide ion supplies evidence for a reaction pathway *via* carbonium ions or ion pairs. The rate constants of the reactions of unsubstituted benzyl chloride must contain contributions of the carbonium ion pathway and, consequently, the experimental isotope effects do not refer to pure SN2 processes.

Some work has been done in this laboratory on kinetic deuterium isotope effects in reactions of methyl iodide with various nucleophiles.[3-5] The present study is concerned with α-deuterium isotope effects in SN2 reactions of a halide with a larger primary alkyl group. A suitable choice is benzyl chloride because of its relatively high reactivity. Furthermore, the presence of the aromatic ring provides the opportunity of studying the influence of remote substituents on the isotope effect. A ring substituent may affect reacting bond orders and force constants in the transition state and cause a noticeable change of the isotope effect.[6]

Previous work on deuterium isotope effects in SN2 reactions of benzyl compounds was carried out by Östman[7] and Strecker and Elias,[8] who studied the chloride ion exchange reaction of benzyl chloride. Hill and Fry[9] investigated the influence of substituents on the chlorine isotope effect in reactions of benzyl chloride with various nucleophiles. Variations in the isotope effect were mainly due to changes in the relative contributions of the SN2 and SN1 mechanisms to the overall reaction.

In this work, the α-deuterium isotope effect has been determined for the reactions of benzyl chloride, *m*-chlorobenzyl chloride, and *p*-methylbenzyl chloride with cyanide ion in 55% (by volume) aqueous Methyl Cellosolve. The investigation has been supplemented by measurements of rate constants of solvolysis of the three benzyl chlorides and their α-dideuterated variants at the same ionic strength (addition of $NaClO_4$ instead of KCN). These rate constants are needed for the treatment of the kinetic data of the reaction with cyanide ion, since solvolysis is a competing reaction. A systematic isotope effect study at a series of different temperatures has been carried out for both reactions of the mentioned three benzyl chlorides. Though further work is necessary in order to establish a noticeable substituent effect on the isotope effect of the SN2 reaction, the results are published now as the authors will not have the opportunity to continue the work in the very near future.

The following parallel reactions occur in a solution containing benzyl chloride and cyanide ion.

$$\mathrm{ArCH_2Cl + CN^- \longrightarrow ArCH_2CN + Cl^-} \quad (k_2)$$

$$\left.\begin{array}{l}\mathrm{ArCH_2Cl + H_2O + CN^- \longrightarrow ArCH_2OH + Cl^- + HCN}\\ \mathrm{ArCH_2Cl + ROH + CN^- \longrightarrow ArCH_2OR + Cl^- + HCN}\end{array}\right\} \quad (k_1)$$

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[2] Address correspondence to author at D 237 Rendsburg, Kampenweg 22, West Germany.

[3] A. V. Willi and C. M. Won, *J. Amer. Chem. Soc.*, **90**, 5999 (1968).

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Strong acid formed in the first-order solvolysis is immediately neutralized by cyanide ion, which is present in excess. Consequently, cyanide ion is consumed in the first-order as well as in the second-order process. This leads to a relatively simple stoichiometric relationship (eq 1 below) (assuming that $[Cl^-]_0 = 0$).

$$[ArCH_2Cl]_0 - [ArCH_2Cl] = [CN^-]_0 - [CN^-] = [Cl^-] \quad (1)$$

In rate eq 2, $[CN^-]$ is substituted with the aid of eq 1, and eq 3 is obtained upon subsequent integration.[10,11]

$$-d[ArCH_2Cl]/dt = k_2[ArCH_2Cl][CN^-] + k_1[ArCH_2Cl] \quad (2)$$

$$Z = \ln \frac{A_0(A + (k_1/k_2) + B_0 - A_0)}{A[(k_1/k_2) + B_0]} = [B_0 - A_0 + (k_1/k_2)]k_2t \quad (3)$$

$$A = [ArCH_2Cl];\ A_0 = [ArCH_2Cl]_0;\ B_0 = [CN^-]_0.$$

As far as the authors know, systematic kinetic studies of the reactions of benzyl chlorides with CN^- have not been carried out previously, except for the measurements reported by Hill and Fry.[9] Certainly, eq 3 has not been applied to kinetic data for the reaction with CN^- prior to this work, though it has been utilized in kinetic studies of reactions of alkyl halides[10] or sulfonic esters[12] with OH^-. The solvolysis kinetics of benzyl chlorides have been studied thoroughly.[13] However, no data have been reported which refer to the same solvent mixture as applied in this study.

Experimental Section

Materials.—Commercial samples of benzyl chloride [bp 51–52° (4 mm), n^{23}D 1.5374], *m*-chlorobenzyl chloride [bp 71–72° (4 mm), n^{21}D 1.5556], and *p*-methylbenzyl chloride [bp 53–54° (3 mm), n^{22}D 1.5331] were purified by repeated fractional distillations under reduced pressure. The purity was checked with the aid of refractive index measurements and gas–liquid chromatography.

Benzyl-α,α-d_2 chloride was prepared as follows.[14] A solution of 20 g (0.15 mol) of methyl benzoate in 200 ml of ether was added, with continuous stirring, over a period of 2 hr, to 4 g (0.095 mol) of $LiAlD_4$ (99% isotopic purity) in 300 ml of ether. The resulting solution was refluxed for an additional 3 hr. Excessive deuteride then was destroyed by 10% sodium hydroxide solution until the precipitate just coagulated and settled. The ether solution was filtered off from the solid and the latter was dissolved in 50 ml of cold 25% sulfuric acid and extracted with two additional portions of ether. The combined ether solution was washed with 10% sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate, and the ether was distilled off. Repeated distillations of the residue under reduced pressure yielded 14.6 g of benzyl-α,α-d_2 alcohol (91% of theory).

Thionyl chloride (30 ml, 0.4 mol) in 30 ml of ether was mixed slowly with 14.6 g (0.133 mol) of benzyl-α,α-d_2 alcohol in 30 ml of ether.[15] The resulting solution was stirred at room temperature for 12 hr. After evaporation of ether and excess thionyl chloride, two consecutive distillations at reduced pressure yielded 14.1 g (83% of theory) of benzyl-α,α-d_2 chloride, bp 48–49 (3 mm), n^{21}D 1.5372. The purity was checked with the aid of gas–liquid chromatography, and dideuteration in the α position (at least 99%) was confirmed by nmr spectroscopy.

m-Chlorobenzyl-α,α-d_2 chloride [bp 68–70° (3 mm), n^{19}D 1.5552] and *p*-methylbenzyl-α,α-d_2 chloride [bp 53–54° (3 mm), n^{22}D 1.5331) were prepared according to the same method, using correspondingly substituted methyl benzoates as starting materials.

Methyl Cellosolve was purified by twofold distillation under a slow stream of nitrogen. A few pieces of sodium metal were added prior to the first distillation.

Water was freshly distilled, and a stream of nitrogen was passed through every sample in order to remove dissolved oxygen.

Kinetic Procedures.—In a typical experiment, *ca.* 0.002 mol of benzyl chloride was dissolved in 55 ml of Methyl Cellosolve in a 100-ml volumetric flask; 10 ml of freshly prepared *ca.* 0.4 *M* potassium cyanide solution was added; and the flask was filled with water to the mark. (In a solvolysis experiment, sodium perchlorate solution was added instead of potassium cyanide solution.) The solution was immediately filled into ampoules. The sealed ampoules were placed into a thermostated water bath with a temperature constancy of ±0.02°. Experiments with corresponding α,α-h_2 and α,α-d_2 compounds were done simultaneously, in the same thermostat. At suitable time intervals, ampoules were taken out, cooled to 20°, opened, and analyzed.

A 10-ml sample of the kinetic solution was mixed with 5 ml of 20% aqueous formaldehyde in order to remove free cyanide ion.[16] (This would not be necessary in the solvolysis experiments.) Nitric acid (6 *N*, 5 ml) and 150 ml of deionized water were added, and chloride ion was determined quantitatively by potentiometric titration with 0.01 *N* silver nitrate solution at a silver–silver chloride electrode, utilizing a mercurous sulfate reference electrode. The end point was taken from the point of the titration curve with the steepest slope. The end point occurred at about 160 mV in all experiments.

The initial concentrations of benzyl chloride in the kinetic solutions were taken from the Cl^- concentrations in samples in which the reaction had been allowed to go to completion. The CN^- concentration of the stock solution was determined with the aid of the Liebig-Déniges method,[17] by titrating with 0.01 *N* silver nitrate solution in the presence of ammonia and using potassium iodide as an indicator.

First-order rate constants of the solvolysis reactions were calculated from the slopes of the straight lines for log $[ArCH_2Cl]$ as functions of time (eq 4), using a computer with a linear regression program.

$$\log [ArCH_2Cl] = \log [ArCH_2Cl]_0 - k_1t/2.303 \quad (4)$$

A preliminary treatment of the experimental data for the reactions with cyanide ion was carried out with the aid of the integrated second-order rate equation (5).

$$\ln([CN^-]/[ArCH_2Cl]) = \ln([CN^-]_0/[ArCH_2Cl]_0) + ([CN^-]_0 - [ArCH_2Cl]_0)k_2t \quad (5)$$

The preliminary k_2 values were used to compute preliminary values of the ratios k_1/k_2, which then were inserted into eq 3 in order to calculate improved k_2 values from the slopes of the lines for Z as functions of time. Results were utilized to compute improved ratios k_1/k_2 which were inserted again into eq 3. This procedure was repeated several times until the k_2 value changed by less than 0.2% when going through one cycle. These calculations were done in a computer with a suitable iterative program which contained as a subroutine a linear regression program for the calculation of the slope of the line according to eq 3.

Results

The initial concentrations of the benzyl chlorides were *ca.* 0.020 *M* in all experiments. In the experiments with the second-order reaction, the initial concentration of CN^- was 0.0416 *M*. In the solvolysis

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TABLE I

SECOND-ORDER RATE CONSTANTS AND ISOTOPE EFFECTS OF THE REACTIONS OF BENZYL CHLORIDES (RCl) WITH CYANIDE ION, CORRECTED FOR PARALLEL FIRST-ORDER SOLVOLYSIS, IN 55% (BY VOL) AQUEOUS METHYL CELLOSOLVE

Reactant	Temp, °C	R = $ArCH_2$, $10^4 k_2$, $sec^{-1} mol^{-1}$ l.	R = $ArCD_2$, $10^4 k_2$, $sec^{-1} mol^{-1}$ l.	k_H/k_D
Benzyl chloride	30.0	1.150	1.121	1.0245 (±0.0010)
	40.0	2.933	2.865	1.023 (±0.007)
	50.0	7.044	6.879	1.0235 (±0.0013)
	60.0	16.03	15.77	1.016 (±0.003)
m-Chlorobenzyl chloride	40.0	2.357	2.370	0.995 (±0.002)
	50.0	5.537	5.528	1.001 (±0.004)
	60.0	12.99	13.07	0.994 (±0.010)
	70.0	28.96	28.87	1.0035 (±0.0035)
p-Methylbenzyl chloride	40.0	(5.567)	(4.409)	1.261 (±0.017)
	50.0	(13.22)	(10.63)	1.246 (±0.014)

TABLE II

FIRST-ORDER RATE CONSTANTS AND ISOTOPE EFFECTS OF THE SOLVOLYSES OF BENZYL CHLORIDES IN 55% (BY VOL) AQUEOUS METHYL CELLOSOLVE IN THE PRESENCE OF 0.0416 *M* $NaClO_4$

Reactant	Temp, °C	R = $ArCH_2$, $10^6 k_1$, sec^{-1}	R = $ArCD_2$, $10^6 k_1$, sec^{-1}	k_H/k_D
Benzyl chloride	30.0	1.223	1.199	1.020 (±0.006)
	40.0	3.556	3.456	1.029 (±0.002)
	50.0	9.698	9.430	1.0285 (±0.0060)
	60.0	24.98	24.37	1.025 (±0.002)
m-Chlorobenzyl chloride	50.0	1.836	1.821	1.007 (±0.018)
	60.0	4.498	4.491	1.002 (±0.006)
	70.0	10.99	11.18	0.984 (±0.004)
p-Methylbenzyl chloride	40.0	27.95	26.75	1.045 (±0.020)
	50.0	77.78	72.80	1.068 (±0.020)

TABLE III

ARRHENIUS PARAMETERS

	Reaction with CN^-		Solvolysis	
Reactant	log *A*	E_a, kcal	log *A*	E_a, kcal
$C_6H_5CH_2Cl$	8.766 (±0.002)	17.62 (±0.04)	8.633 (±0.003)	20.18 (±0.07)
$C_6H_5CD_2Cl$	8.793 (±0.003)	17.68 (±0.06)	8.601 (±0.005)	20.15 (±0.11)
m-$ClC_6H_4CH_2Cl$	8.867 (±0.009)	17.92 (±0.19)	7.626 (±0.010)	19.77 (±0.20)
m-$ClC_6H_4CD_2Cl$	8.842 (±0.010)	17.88 (±0.24)	7.798 (±0.010)	20.03 (±0.31)
p-$CH_3C_6H_4CH_2Cl$			9.78 (±0.02)	20.55 (±0.49)

experiments, the solutions contained 0.0416 *M* sodium perchlorate in order to maintain the same ionic strength as in the experiments with the second-order reaction.

Second-order rate constants and α-deuterium isotope effects of the reactions of benzyl chlorides with CN^- are reported in Table I. Each value is the average of three separate determinations. Results of k_2 for the reaction of *p*-methylbenzyl chloride are in parentheses because they probably do not refer to real second-order processes. First-order rate constants and α-deuterium isotope effects of the solvolysis reactions of benzyl chlorides are collected in Table II. Each value is the average of two separate determinations. Standard deviations of the isotope effects are given in both tables.

It is also possible to calculate first-order rate constants for the overall reaction of *p*-methylbenzyl chloride in the presence of CN^-. Their values at 50° are 1.174×10^{-4} sec^{-1} for $CH_3C_6H_4CH_2Cl$ and 1.031×10^{-4} sec^{-1} for $CH_3C_6H_4CD_2Cl$. Subtraction of the corresponding first-order solvolysis rate constants leads to the following value of the α-deuterium isotope effect on the rate increase in the presence of CN^-: $k_H/k_D = 3.96 \times 10^{-5}/3.03 \times 10^{-5} = 1.31$ (±4%) (estimated precision). This result is in approximate agreement with the value based on apparent second-order constants (Table I).

Rate constants are decreased by *m*-Cl and increased by *p*-CH_3 at the ring in the reaction with CN^- as well as in the solvolysis. Both series lead to poor Hammett relationships no matter whether σ or σ^+ is applied.

The α-deuterium isotope effect is equal to unity within experimental error in both reactions of *m*-chlorobenzyl chloride, and it is *ca.* 1.02 in both reactions of benzyl chloride. The value of k_H/k_D is just a little higher in the solvolysis of *p*-methylbenzyl chloride; it is unusually high in the reaction of the *p*-methyl compound with CN^-.

Arrhenius parameters of the rate constants are reported in Table III. The Arrhenius parameters of the α-deuterium isotope effect in the reaction of *m*-chlorobenzyl chloride with CN^- are $A_H/A_D = 1.069$ (±0.006) and $E_{aH} - E_{aD} = 45$ (±48) cal. It has not been possible to obtain reliable Arrhenius parameters for the isotope effect in the solvolysis of *m*-chlorobenzyl chloride because the temperature interval of the data is only 20°. (The experimental Arrhenius parameters of the isotope effects in both reactions of benzyl chloride are irrelevant, as it is likely that neither k_2 nor k_1 is governed by one single mechanism.)

Discussion

The α-deuterium isotope effects in the reactions of benzyl chloride and *m*-chlorobenzyl chloride with cyanide ion and in the solvolyses of all three compounds studied are in the range of values found for S_N2 reactions (0.95 to 1.04 per α-D).[3-5,7,8,18-20] These findings indicate that the main reaction pathway in the solvolyses of all three compounds involves nucleophilic participation of solvent.[21]

The α-deuterium isotope effect in the reaction of *p*-methylbenzyl chloride with cyanide ion is much higher. The value based on the increase of the first-order rate constant ($k_H/k_D = 1.31$) is almost identical with the result obtained by Shiner, *et al.*,[21] for the limiting solvolysis of *p*-methylbenzyl chloride in 70% aqueous trifluoroethanol: $k_H/k_D = 1.14$ per α-D (or 1.30 per two α-D). Consequently, the reaction of *p*-methylbenzyl chloride with CN^- must pass through a carbonium ion like transition state.[22] Further evidence for rate-determining carbonium ion formation is supplied by the adherence of the overall reaction to the first-order rate law and by Hill and Fry's observation that the first-order rate constants of the reactions of *p*-methylbenzyl chloride with CN^- and $S_2O_3^-$ are nearly equal.[9]

It can be expected that the carbonium ion reacts much faster with the stronger nucleophiles CN^- or $S_2O_3^{2-}$ than with Cl^-. (Reaction with Cl^- is the reversal of the first step in the mechanism.) In such a case, formation of the carbonium ion (or possibly an ion pair) becomes rate-determining. If, on the other hand, no strong nucleophile is present (solvolysis experiments), return from the carbonium ion to *p*-methylbenzyl chloride appears to be more important than reaction with solvent. The rate of reaction *via* the carbonium ion pathway then is decreased, and the parallel one-step S_N2 reaction with solvent prevails.

Equation 6 is derived with the aid of the method of

$$k = \frac{k_I(k_{solv} + k_{CN}[CN^-])}{k_{-I}[Cl^-] + k_{solv} + k_{CN}[CN^-]} + k'_{SN2} + k^{CN}_{SN2}[CN^-] \qquad (6)$$

the stationary state. k_I is the rate constant of carbonium ion formation from RCl; k_{-I}, k_{solv}, and k_{CN} are the rate constants of the reactions of the carbonium ion intermediate with Cl^-, solvent, and CN^-, respectively. k'_{SN2} is the pseudo-first-order rate constant of the S_N2 reaction of RCl with solvent; k^{CN}_{SN2} is the rate constant of the S_N2 reaction of RCl with CN^-. (The order of the overall reaction still may be unity within experimental error if k^{CN}_{SN2} is relatively small though not negligible.) A more complicated equation must be applied if ion pair intermediates are to be considered in addition. However, there are not enough data available for a more thorough treatment.

If the CN^- concentration is large enough, eq 6 becomes eq 6b.

$$k_{CN}[CN^-] \gg k_{-I}[Cl^-] + k_{solv}$$
$$k = k_I + k'_{SN2} + k^{CN}_{SN2}[CN^-] \qquad (6b)$$

In the solvolysis experiments, on the other hand, $[CN^-] = 0$ and eq 6 reduces to eq 7.

$$k = \frac{k_I}{1 + (k_{-I}/k_{solv})[Cl^-]} + k'_{SN2} \qquad (7)$$

It is important to know whether the carbonium ion mechanism contributes to the overall reactions of benzyl chloride and *m*-chlorobenzyl chloride with CN^- or solvent. Estimates of k_I for the unsubstituted and *m*-Cl compounds may be obtained from the k_I value of the *p*-CH_3 compound by application of the Hammett relationship.

The ρ value for the solvolyses of substituted phenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25° is -4.62;[23] ρ values in the range of -4.05 to -4.63 have been found for the solvolyses of substituted benzhydryl chlorides in various solvents.[24] The more polar the solvent, the stronger is the substituent effect. Furthermore, ρ values of -4.41 and -4.39 can be calculated from the data obtained by Hill and Fry[9] in 80% aqueous dioxane for the reactions of *p*-methylbenzyl chloride and *p*-methoxybenzyl chloride with CN^- and $S_2O_3^{2-}$, respectively. Consequently, a good estimate for the ρ value in the carbonium ion formation of substituted benzyl chlorides under the experimental conditions of this work is -4.4.

The overall first-order constant of the reaction of *p*-methylbenzyl chloride in the presence of CN^- includes contributions of S_N2 reactions with solvent and CN^-. On the other hand, the contribution of the carbonium ion mechanism still may be a little smaller than k_I. Therefore, k_I is assumed to be approximately equal to the measured overall first-order rate constant, $k = 1.17 \times 10^{-4}$ sec^{-1} at 50°.

According to the observed isotope effect in the solvolysis of *p*-methylbenzyl chloride, approximately one-third (or less) of the measured rate constant corresponds to the carbonium ion mechanism: $7.78 \times 10^{-5}/3 = 2.59 \times 10^{-5}$ sec^{-1}. With the aid of eq 7, the following result is obtained.

$$1 + (k_{-I}/k_{solv})[Cl^-] = 1.17 \times 10^{-4}/2.59 \times 10^{-5} = 4.52.$$

(Since $[Cl^-]$ is variable, this is merely an average value which refers to initial concentrations of RCl near 2×10^{-2} *M*.)

The following estimates of k_I (at 50°) are computed from the Hammett relationship (application of σ^+): 5.55×10^{-6} sec^{-1} for benzyl chloride and 1.30×10^{-7} sec^{-1} for *m*-chlorobenzyl chloride.

If it is assumed that the same value of $1 + (k_{-I}/k_{solv})[Cl^-]$ may be utilized for the three compounds studied, the estimates of the first term in eq 7 (which corresponds to the carbonium ion mechanism) are 1.2×10^{-6} sec^{-1} for the unsubstituted compound and 2.9×10^{-8} sec^{-1} for the *m*-Cl compound. By comparison with the experimental solvolysis rate constants (Table

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[20] S. Seltzer and A. A. Zavitsas, *ibid.*, **45**, 2023 (1967), and references cited therein.

[21] V. J. Shiner, M. W. Rapp, and H. R. Pinnick, *J. Amer. Chem. Soc.*, **92**, 232 (1970); V. J. Shiner, M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, **90**, 7171 (1968).

[22] It is suggested that the constancy of the value of k_H/k_D per α-D in limiting solvolysis reactions does not necessarily mean that the bond between carbon and leaving group must be completely broken. If the transition states are carbonium ion like with incomplete bond cleavage (as in S_N1 reactions), 90% bond cleavage in one individual example and 93% in another would cause only a small difference in the isotope effect. Therefore, a constant isotope effect in different examples with the same leaving group is not incompatible with an S_N1 mechanism *via* free carbonium ions.

[23] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[24] Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4969 (1958).

II), it is concluded that the carbonium ion mechanism may account for *ca.* 12% (high estimate) of the solvolysis rate of benzyl chloride while it is negligible (1.6% or less) in the solvolysis of *m*-chlorobenzyl chloride.[25] It is obvious that there is an appreciable contribution of the carbonium ion mechanism in the solvolysis of *p*-methylbenzyl chloride.

In order to estimate the contributions of the carbonium ion mechanism to the reactions with CN^-, calculated values of k_I are compared with experimental values of $k_2(B_0 - A_0)$. According to these comparisons, the carbonium ion pathway may account for an appreciable fraction of the reaction rate of benzyl chloride with CN^-, but it is negligible (*ca.* 1% or less) in the reaction of *m*-chlorobenzyl chloride with CN^-.

Conclusions

The first goal of this study was the determination of α-deuterium isotope effects in SN2 reactions of a benzyl chloride. The data obtained for the reaction of *m*-chlorobenzyl chloride with CN^- and the solvolysis of *m*-chlorobenzyl chloride refer to practically pure S_N2 reactions. Results of k_H/k_D per α-D are a little higher than in the reaction of methyl iodide with CN^- (k_H/k_D = 0.97 per α-D)[3] or in the solvolysis of methyl iodide (k_H/k_D = 0.955 per α-D).[18] This corresponds to findings for other S_N2 processes in which isotope effects in reactions of methyl iodide and methyl chloride with the same nucleophile are compared.[20]

It is planned to carry out sample calculations of isotope effects from force constants at a later date. It will be necessary to consider solvation of the entering and leaving groups in the transition state model.[5]

The observed increases of k_H/k_D when going from the *m*-chloro to the unsubstituted compound must be due to an increased contribution of the parallel reaction *via* the carbonium ion pathway. It is very difficult to arrive at reliable quantitative estimates of the contributions of the carbonium ion mechanism. It even may be possible that decreasing electron-withdrawing power of the ring substituent would cause *decreases* of the values of k_H/k_D in the S_N2 reactions.

In order to obtain reliable information about the substituent effect on the isotope effects in the S_N2 reactions, it will be necessary to study the reactions of benzyl chlorides containing stronger electron-withdrawing substituents, such as *p*-CN, *m*-NO_2, and *p*-NO_2.

An unexpected side result is the occurrence of the carbonium ion mechanism in the reaction of *p*-methylbenzyl chloride with CN^-. It may be worthwhile to carry out a detailed study of this reaction in which $[Cl^-]$ and $[CN^-]$ are varied while the ionic strength is kept constant.

Registry No.—Cyanide ion, 57-12-5; benzyl chloride, 100-44-7; *m*-chlorobenzyl chloride, 620-20-2; *p*-methylbenzyl chloride, 104-82-5; benzyl-α,α-d_2 chloride, 33712-34-4; *m*-chlorobenzyl-α,α-d_2 chloride, 33712-35-5; *p*-methylbenzyl-α,α-d_2 chloride, 33712-36-6.

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[25] A reviewer inquired about the possibility of α elimination as a side reaction.

It may be desirable to confirm experimentally the absence of α-elimination products in the reactions studied in this work. However, evidence for the insignificance of *base-promoted α elimination* was supplied by Bunnett and Reinheimer[26] for the reaction of *o*-chlorobenzyl chloride with LiOMe in MeOH. The present study is concerned with benzyl chlorides carrying groups with comparable or weaker electron-withdrawing power. It can be concluded that base-promoted α elimination is even less likely under the action of a weak base such as CN^-.

Furthermore, it is completely nonessential for the kinetics if some benzyl cyanide (instead of alcohol) is formed also on the S_N1 pathway, since it concerns the product-forming rather than the rate-determining step. Determination of the benzyl cyanide product ratio merely would supply a high limit of the relative contribution of the S_N2 reaction with CN^-.

[26] J. F. Bunnett and J. D. Reinheimer, *J. Amer. Chem. Soc.*, **84**, 3287 (1962).

Kinetic Study of the Oxidation of *p*-Nitrosophenol by Nitric and Nitrous Acids

ALBRECHT GRANZOW AND ABRAHAM WILSON*

Research and Development Department, Organic Chemicals Division, American Cyanamid Company,
Bound Brook, New Jersey 08805

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The acid-catalyzed oxidation of *p*-nitrosophenol by nitric and nitrous acid in aqueous sulfuric acid solution has been studied kinetically in the acidity region of $-1 > H_0 > -6$ by means of polarographic and iodometric analysis. The experimental rate law is first order with respect to *p*-nitrosophenol, nitric acid, and nitrous acid. At low initial nitrous acid concentrations, autocatalysis is observed. The acidity profile of the rate constant has a maximum at $H_0 = -4.5$. The uv absorption of *p*-nitrosophenol is acidity dependent, which is in accordance with a protolytic equilibrium between *p*-nitrosophenol and its conjugate acid. The acidity at which half-protonation occurs is $H_0 = -3.7$. A possible reaction mechanism is discussed which assumes a rate-limiting attack of dinitrogen tetroxide on *p*-nitrosophenol in the low acidity region. At high acidities deprotonation of a reaction intermediate may become rate limiting.

The nitric acid oxidation of *p*-nitrosophenol was first studied by Veibel.[1] He reported a pseudo-first-order rate law with respect to *p*-nitrosophenol, the rate constant being strongly enhanced by an increase of the nitric acid concentration. The reaction was found to occur only if a small amount of nitrous acid was initially present. More recently, Ogata and coworkers have investigated the nitric acid oxidation of various aromatic nitroso compounds with aqueous dioxane as a solvent. In the case of nitrosobenzene,

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[1] S. Veibel, *Z. Phys. Chem., Abt. B.*, **10**, 22 (1930).