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Secondary Kinetic Isotope Effects in Bimolecular Nucleophilic Substitutions. VI. Effect of α and β Deuteration of Alkyl Halides in their Menschutkin Reactions with Pyridine in Nitrobenzene¹

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A survey of kinetic, secondary deuterium isotope effects, for α , β , and γ deuterated alkyl halides reacting with pyridine in nitrobenzene solvent has been made. α -Deuterium effects have been measured for eight compounds, β -deuterium effects for four compounds, and one rate ratio for γ -deuteration is reported. The possible errors in the rate ratios for β -deuterated compounds, resulting from the elimination side reaction have been determined. The results are discussed in terms of transition state structure.

Une étude sur la cinétique des effets isotopiques secondaires du deutérium a été effectuée sur les halogénures d'alkyle α , β , et γ deutérés qui réagissent avec la pyridine dans le nitrobenzène. Les effets du deutérium en α ont été mesurés au moyen de huit composés, les effets du deutérium en β au moyen de quatre composés, et on rapporte un rapport de vitesse pour la deutération en γ . Les erreurs possibles dans les rapports de vitesse pour les composés β -deutérés, et qui résultent d'une réaction annexe d'élimination, ont été déterminées. Les résultats sont discutés en fonction de la structure de l'état de transition.

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Introduction

Although many secondary deuterium isotope effects have been measured for nucleophilic substitutions at saturated carbon, systematic studies involving changes in the leaving group, the alkyl group, and the position of deuteration are not common. Robertson and co-workers (1-4) have provided the most complete set of data for solvolysis reactions in water of alkyl halides and sulfonates, and Brown and McDonald (5) have reported a series of measurements on various substituted deuterated pyridines reacting with alkyl iodides in nitrobenzene solvent. This paper presents a set of isotopic rate ratios for the reaction of a single nucleophile pyridine, with various deuterated alkyl compounds in the same solvent, nitrobenzene.

Results and Discussion

a-Deuterium Effects

In Table 1 the second-order rate constants and isotopic rate ratios are shown for α -deuterated alkyl iodides, bromides, and tosylate. The

reactions were followed conductometrically for all but the methyl bromide reaction, for which the sealed tube technique was used with analysis for bromide ion by titration. All of the rate constants are at 50 °C, except for ethyl bromide, which was run at 35 °C.

The result of changing the leaving group from iodide, to bromide, to tosylate is to decrease the isotope effect, *i.e.* to bring the rate ratio closer to unity. This change is analogous to the behavior of methyl compounds solvolyzing in water (1) and if the rate ratios are plotted against $E_n - E_l$, where E_n is the Edward's nucleophilicity factor (6, 7) of the incoming nucleophile and E_1 that of the leaving group, the three points yield a line parallel but not coincident with the one plotted by Seltzer and Zavitsas (8, 9). The order magnitude of the isotope effect (I > Br > OTs for inverse effects or OTs > Br > I for normal effects) has been explained (10, 11) for limiting solvolytic reactions proceeding via ion-pairs, in terms of the effect of the leaving group on the initial state. However, the non-solvolytic Menschutkin reaction is known to pass through an S_N2 transition state, and this transition state might be expected to yield a significant contribution to the isotope effect. In another nonsolvolytic reaction, that of thiosulfate ion with methyl- d_3 iodide, bromide, and tosylate, the rate ratios contrast with the series above in

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Alkyl compound	$10^6 k_{\rm H}$ (1 mol ⁻¹ s ⁻¹) (± standard error)	$10^6 k_{\rm D}$ (l mol ⁻¹ s ⁻¹) (± standard error)	$k_{\rm H}/k_{\rm D}$ (± standard error)	$(k_{\rm H}/k_{\rm D})$ per D
Methyl iodide*	$2038 \pm 17*$	2287 ± 8*	$0.891 \pm 0.008*$	0.96,
Methyl bromide	968 ± 3	1043 ± 3	$0.92_8 \pm 0.003$	0.975
Methyl tosylate	715.3 ± 4	727.8 ± 7	$0.98^{\circ}_{2} + 0.01$	0.99
Ethyl iodide	151.5 ± 0.1	$156_{2} \pm 0.3$	$0.96_{7} \pm 0.003$	0.98
Ethyl bromide [†]	$8.8_8 \pm 0.05^{\dagger}$	$9.1_8 \pm 0.03^{\dagger}$	$0.96_7 \pm 0.006^{\dagger}$	0.98,
<i>n</i> -Propyl bromide	$13.2_6 \pm 0.15$	13.81 ± 0.15	$0.96_0 \pm 0.015$	0.98
Isopropyl iodide‡	$9.44_{4} \pm 0.011$	$9.40_5 \pm 0.011$	$1.00_4 \pm 0.002 \pm$	1.004
Isopropyl bromide	$0.95_2 \pm 0.009$	$0.99_{3} \pm 0.011$	$0.95_8 \pm 0.014$	0.958

TABLE 1.	Second-order rate constants and α -deuterium isotope effects for reactions of alkyl compounds			
with pyridine at 50.0 $^{\circ}$ C in nitrobenzene solvent				

Reference 17

[†]Rate constants measured at 35.02 °C. [‡]Rate constants measured at 49.92 °C.

giving values of 1.058, 1.031, and 1.12, respectively (9).

The ethyl- αd_2 iodide and bromide reactions give exactly the same rate ratio of 0.967 and isopropyl- αd_1 iodide gives a more normal ratio than the corresponding bromide. Thus the change in isotope effect between iodide and bromide leaving groups depends upon the alkyl radical and, therefore, is probably related to a large extent to the control of the transition state structure by the alkyl radical.

The trend towards a normal (>1) rate ratio with α -methylation of the alkyl group for a constant leaving group is also observed in Table 1 and appears to be a general phenomenon (1, 2). This has been interpreted in zero-point energy terms, assuming that the ΔH^{\dagger} isotope effect dominates that of ΔS^{\dagger} , which is true for several $S_N 2$ reactions (12–14). The argument is that a tight $S_N 2$ transition state, such as that for a methyl compound leads to an increase in the C—H bending frequencies during activation, which in turn leads to a faster rate for the deuterium compound than for the protium compound (15). A looser transition state resulting from charge delocalization within a carbon skeleton such as an isopropyl group, yields less increase (or in some cases a decrease) in the C—H (C—D) bending modes of vibration on going from the initial to the transition state and therefore a smaller inverse isotope effect. This implies that for isopropyl compounds, bond breaking is more important than bond making and that the entering and leaving groups are held, presumably by the steric effects of the methyl groups, at a greater distance from the

 α -C—H (or C—D) bond, which would, therefore, be relatively free in the transition state with respect to the bending vibrations. Thus the methyl halides have tighter transition states than ethyl or isopropyl halides and larger inverse isotope effects and, of the two halides, the larger iodide has the greater inhibition of the C-H and C-D bending vibrations in the transition state and hence the larger inverse isotope effect. For the methyl compounds, the more polarizable the leaving group, I > Br >OTs on the Edwards E scale (6, 7), the greater will be the degree of bond making in the transition state and hence the more crowded it will be, giving rise to a larger isotope effect.

The inverse isotope effect observed with isopropyl- αd_1 bromide may be due to the fact that a larger excess (eightfold) of nucleophile was used for this compound than for the others, which was necessitated by practical reasons. With such a large excess of pyridine the reaction tends to be a pyridinolysis, since the pyridine will tend to solvate the transition state preferentially, compared to nitrobenzene. This effective change to a solvent of more specific solvating power (16) will give a transition state for the reaction more reactant-like (17) and therefore more crowded with a larger isotope effect.

β -Deuterium Effects

Secondary β -deuterium isotope effects in S_N2 reactions present a problem in that some amount of E2 side reaction usually occurs concurrently and the elimination of a β -hydrogen (or deuterium) in the E2 reaction introduces a primary deuterium isotope effect of large magni-

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lsopropyl halide	10 ³ [HX]* (mol 1 ⁻¹)	$10^{3}[X_{2}]^{*}$ (mol l ⁻¹)	10 ³ [X ⁻]* (mol 1 ⁻¹)	$\frac{100 \times E2}{E2 + S_N 2}$ (%)†
Iodide	0.668	0.141	47.45	2.0
Bromide	0.707		94.82	0.74

[1]

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TABLE 2. Product analyses and the percentage of elimination in the reactions of isopropyl halides with pyridine in nitrobenzene at 50 °C

 $X \equiv Halogen$

†Calculated from $\frac{100([HX] + 2[X_2])}{(HX)}$

 $[X^{-}] + 2[X_{2}]$

tude, typically a factor of 4 to 8 for the rate ratio (18, 19) although much larger values have been observed (20-22).

While the percentage of E2 to the total reaction is expected to be small for the quaternization reaction (23), it is apparent that even a small percentage could give rise to misleading, small, overall normal isotope effects. In order to determine the magnitude of this source of error a careful product analysis was carried out for the reactions of isopropyl iodide and bromide, for which the E2 side reaction is known to be larger than for the ethyl and *n*-propyl halides (24). The total product formed was obtained by potentiometric titration with aqueous silver nitrate and the elimination products were estimated by a non-aqueous acid-base titration following Brown and Cahn (25) plus, in the case of the iodide, a spectrophotometric determination of iodine which was presumed to have been formed by oxidation of some of the hydriodic acid (25). The analytical results are compiled in Table 2. As expected, the proportion of elimination is greater for the iodide than for the bromide (24). The value of $2\frac{1}{\sqrt{6}}$ for the iodide may be compared with Brown and Cahn's approximate figure (25) of 3% for equal initial molar concentrations of methyl substituted pyridines and isopropyl iodide in the same solvent.

The possible error introduced into the secondary isotope effect by the elimination reaction may be estimated as follows:

> $S_N 2$ rate = $k_s [RX] [C_5 H_5 N]$ E2 rate = $k_{\rm E}[{\rm RX}][C_5{\rm H}_5{\rm N}]$ Observed rate = $k_{obs}[RX][C_5H_5N]$ $= (k_{\rm E} + k_{\rm s})[{\rm RX}][{\rm C}_{5}{\rm H}_{5}{\rm N}]$

$$\left(\frac{k_{\rm H}}{k_{\rm D}}\right)_{\rm obs} = \frac{k_{\rm E}^{\rm H} + k_{\rm s}^{\rm H}}{k_{\rm E}^{\rm D} + k_{\rm s}^{\rm D}}$$

If the secondary isotope effect, $k_s^{\rm H}/k_s^{\rm D}$, is assumed to be unity and the primary isotope effect $k_{\rm E}^{\rm H}/k_{\rm E}^{\rm D}$ is written 'x', eq. 2 is obtained by dividing the numerator and denominator of eq. 1 by $k_{\rm E}^{\rm D}$.

2]
$$\left(\frac{k_{\rm H}}{k_{\rm D}}\right)_{\rm obs} = \frac{x(k_{\rm s}^{\rm H}/k_{\rm E}^{\rm H}+1)}{x.k_{\rm s}^{\rm H}/k_{\rm E}^{\rm H}+1}$$

The numerical value of $k_{\rm s}^{\rm H}/k_{\rm E}^{\rm H}$ for isopropyl iodide and bromide may be calculated from the figures in Table 2 as 49 and 133, respectively.

The observed rate ratio for isopropyl iodide, assuming no secondary isotope effect and a typical primary isotope effect (x = 7) would be $(k_{\rm H}/k_{\rm D})_{\rm obs} = 1.017$ and the largest possible ratio (x = 700) would be 1.020. For isopropyl bromide primary isotope effects of 7 and 700 would give rate ratios of 1.006 and 1.007. Therefore, for these small amounts of elimination the maximum error is about the same percentage as the elimination is of the total reaction.

Second-order rate constants for some β -deuterated alkyl halides and their isotopic rate ratios are shown in Table 3. In determining the isotope effects, the normal compound was always run simultaneously with the deuterated sample to eliminate errors such as temperature fluctuation and where the α and β effects were measured at widely separated time intervals, slight differences in $k_{\rm H}$ are noted. The corrected rate ratio was calculated assuming a primary isotope effect on the elimination reaction of 7. The elimination percentage was not investigated for the ethyl and *n*-propyl halides since it is expected to be very small indeed for these compounds (24).

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	$10^{6}k_{\rm H}(1 \text{ mol}^{-1} \text{ s}^{-1})$ (± standard error)	$10^6 k_{\rm D} (1 \text{ mol}^{-1} \text{ s}^{-1})$ (\pm standard error)	$k_{\rm H}/k_{\rm D}$ (observed)	$k_{\rm H}/k_{\rm D}^*$ (corrected)	$(k_{\rm H}/k_{\rm D})$ per D (corrected)
Ethyl iodide	151.5 ± 0.1	149.6 ± 0.9	$1.01_3 \pm 0.006$		1.004
n-Propyl bromide	13.26 ± 0.15	13.23 ± 0.14	$1.00_2 \pm 0.015$		1.00
Isopropyl iodide	9.66 ± 0.04	9.23 <u>+</u> 0.04	$1.04_7 \pm 0.006$	1.03 ₀	1.005
Isopropyl bromide	0.972 ± 0.008	0.885 ± 0.005	$1.09_9 \pm 0.011$	1.09 ₁	1.01 ₅

TABLE 3. Second-order rate constants and isotopic rate ratios for the reaction of β -deuterated alkyl halides with pyridine at 50.0 °C in nitrobenzene solvent

*Corrected assuming a primary isotope effect of 7 for the elimination reaction.

The results in Table 3 show that only in the isopropyl halides is the β -deuterium isotope effect significant, with the bromide giving a rate decrease with deuteration three times larger than the iodide. The direction and magnitude of the effects are not surprising in comparison to those observed in the water solvolysis reactions (4). Since the hydrolysis reactions give a temperature independent isotope effect for isopropyl compounds (26), it is not possible to specify the origin of the isotope effects in the pyridine reaction. However, that normal effects are observed does allow the conclusion that within the S_N^2 mechanism there is a trend to a less crowded (or possibly a more S_N1-like) transition state for secondary compounds than for primary compounds, since this type of structure is required for normal isotope effects whether the explanation is made in terms of the hyperconjugative effects (27) or in terms of internal rotational contributions (26, 28).

The greater magnitude of the rate change for the bromide leaving group than for the iodide again indicates, as found for the α -effect that the iodide has a tighter, more crowded transition state. This trend is in agreement with the β -effect observed by Strecker and Elias (29) for the radiochloride exchange with isopropyl chloride $(k_{\rm H}/k_{\rm p} = 1.12)$.

y-Deuterium Effect

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The relative rates of reaction were measured for *n*-propyl- γd_3 bromide and its normal analogue giving 13.32 and 13.26 × 10⁻⁶ 1 mol⁻¹ s⁻¹ respectively, possibly an inverse isotope effect of about $\frac{1}{2}$ %, but the two rates are barely significantly different. This result is very similar to the γ -effect observed for *n*-propyl- γd_3 bromide reacting with thiosulfate ion (30) in 50% v/v ethanol-water $k_{\rm H}/k_{\rm D} = 0.990$ and very much smaller than the 8% inverse effect found for the same compound solvolyzing in water (3).

From these three results there appears to be an approximate correlation between the β and γ isotope effects with the β rate ratio becoming larger than unity as the γ rate ratio becomes less than unity. This suggests that both these effects depend on transition state geometry and is in accord with the earlier explanations (3), which postulated that the greater the β -hydrogen atom interaction with the central carbon atom p-orbital in the transition state (hyperconjugation), the greater would be the steric inhibition of the vibrations of the γ -hydrogens. The amount of hyperconjugation will be directly related to the degree of incipient positive charge on the central carbon atom in the transition state. Thus, for the three $S_N 2$ reactions of *n*-propyl bromide, it may be concluded that the pyridine reaction has no such charge (or no S_N1 character or no ion-pair character), the thiosulfate ion reaction has a very small amount, and the hydrolysis a slightly larger amount.

Experimental

Materials

Nitrobenzene solvent was dried over anhydrous calcium sulfate and distilled at atmospheric pressure, boiling range 210.5-211 °C. Pyridine was dried with potassium hydroxide pellets and then with calcium hydride before fractional distillation. Material boiling between 115.2 and 115.7 °C was collected and stored in an opaque container over calcium hydride and under nitrogen.

Methyl bromide, previously cooled to -80° in an acetone– Dry Ice slurry was allowed to volatilize at $25-30^{\circ}$, passed through wash towers of concentrated sulfuric acid and glass wool, and collected and stored at -80° . All the other alkyl halides were dried over anhydrous calcium sulfate and fractionally distilled, after which they were stored in opaque containers in an atmosphere of nitrogen and over copper. Methyl tosylate was distilled under vacuum. Commercial samples of methyl- d_3 bromide, ethyl- αd_2 iodide and bromide, *n*-propyl- αd_2 bromide, *n*-propyl- βd_2 bromide, isopropyl- βd_6 iodide and bromide, and *n*-propyl- γd_3 bromide were used without further purification. Commercial methyl- d_3 iodide was redistilled and stored in opaque sealed tubes. Methyl- d_3 tosylate, prepared by Jackson (9), was redistilled under vacuum. Ethyl- βd_3 iodide was prepared by reaction of ethyl- βd_3 tosylate (0.01 mol) with a slurry of dry potassium iodide (0.03 mol) in diethylene glycol (2 ml). The product was distilled from the reaction mixture at 45–50 °C under reduced pressure and collected in a liquid N₂ trap. After several redistillations the ethyl- βd_3 iodide was stored in an opaque sealed tube, under nitrogen, over copper. The yield was 59%. The absence of hydrogen on the β -carbon atom was confirmed by n.m.r. spectroscopy.

Isopropyl- αd_1 halides were prepared from isopropyl- αd_1 alcohol (Merck, Sharp & Dohme Ltd.) via the *p*-bromobenzenesulfonate (brosylate). The general method of Sekera and Marvel (31) was used to convert the alcohol to the brosylate, by reaction with *p*-bromobenzenesulfonyl chloride in anhydrous pyridine at -5 °C. A 57% yield of brosylate was obtained, melting at 31-32 °C. Isopropyl- αd_1 brosylate was converted to the iodide and bromide by reaction with the appropriate solid potassium halide, as described for ethyl- βd_3 iodide. Crude yields of about 60% were obtained and the halides were purified for kinetic work by g.l.c. using a very low column temperature. The deuteration of the compounds was confirmed by the n.m.r. spectra.

Analyses for Elimination Products

Ten sealed tubes each containing 4.402 ml of reaction mixture were prepared and allowed to react at 50° for about ten half-lives. For the isopropyl iodide reaction the substrate concentration was 0.0483 M and that of the pyridine 0.227 M, with a reaction time of 39 days. The corresponding figures for the isopropyl bromide reaction were 0.0973, 0.778 M, and 117 days. The total halide concentrations were determined by potentiometric titration against standard silver nitrate solution of approximately the same molarity as that of the pyridinium halide. Sharp end-points were obtained using wet acetone as solvent. Both reactions were found to be about 98% complete with respect to the isopropyl halide.

The hydrohalic acid concentrations were determined by potentiometric titration of the sample against potassium hydroxide in isopropanol solvent under an atmosphere of nitrogen. Blank titrations were run and the analyses corrected.

In the isopropyl iodide reaction a visible concentration of iodide was produced and this was estimated spectrophotometrically. A calibration curve of \log_{10} (% transmittance), at a wavelength of 480 nm, vs, iodine concentration was set up by preparing solutions of iodine in a mixture of N-ethylpyridinium iodide and pyridine in nitrobenzene. This graph was linear. The ethyl product was used to stimulate the reaction mixture rather than the isopropyl compound because solutions of isopropylpyridinium iodide tend to redden on standing. Thus the iodine concentration recorded in Table 2 may have come from some decomposition of the substitution product as well as the elimination reaction, and the percentage elimination is, therefore, a maximum figure.

Kinetic Measurements

The runs were followed conductometrically in a manner very similar to that previously described (17), except for those involving methyl bromide. A calibration curve was constructed for each alkyl halide reaction and they were all very similar in form to that for trimethylphenylammonium tosylate in nitrobenzene (14). The conductivities were converted to concentrations and the second-order rate constants were calculated from the integrated second-order equation. The kinetics were followed to various reaction percentages up to 50% for most of the alkyl halides, but only up to 10% for the isopropyl compounds. The pyridine was always in excess, ranging from a factor of 2 to a factor of 8. The methyl bromide runs were carried out using a sealed

tube technique, similar to that described previously (28).

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