endo-alcohol were detectable. The infrared spectra[17] also failed to reveal the presence of any significant amount of endo isomer. The reference spectra used in drawing this conclusion were obtained on a mixture of the *endo*- and *exo*-alcohols, with the former predominating, prepared by lithium aluminum hydride reduction of (±)-**5**.[17] On addition of Eu(thd)$_3$ to C^{2}HCl$_3$ solutions of this mixture, the overlapping carbinol ^{1}H NMR peaks at δ 3.5–3.8 (broad, endo) and 3.75 (sharp, exo) ppm gave well-separated peaks in the 12–15-ppm region. The endo peak was shifted by δ 1–1.1 ppm more to lower field than the corresponding exo resonance; their relative integrated intensities were 77:23, respectively.

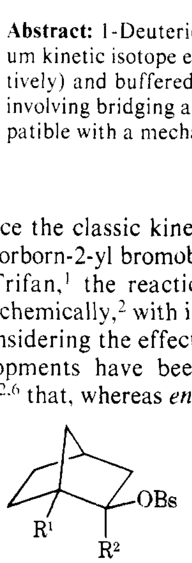
Secondary Deuterium Kinetic Isotope Effects and the Intervention of Nonclassical Ions in the Solvolysis of *exo*-Norborn-2-yl Bromobenzene-*p*-sulfonate

H. Maskill

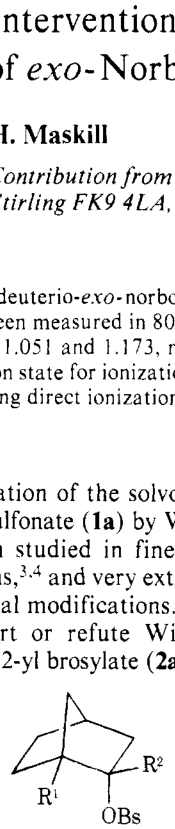
Contribution from the Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland. *Received November 5, 1975*

Abstract: 1-Deuterio- and 1,2-dideuterio-*exo*-norborn-2-yl bromobenzene-*p*-sulfonates have been prepared, and the deuterium kinetic isotope effects have been measured in 80% aqueous ethanol ($k^{\mathrm{H}}/k^{\mathrm{D}}$ = 1.081, 25.5 °C, and 1.192, 25.4 °C, respectively) and buffered acetic acid (1.051 and 1.173, respectively, 29.4 °C). These results are in accordance with a mechanism involving bridging at the transition state for ionization which leads to the nonclassical norbornyl cation. The results are incompatible with a mechanism involving direct ionization to interconverting classical cations.

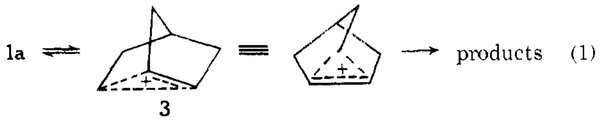
Since the classic kinetic investigation of the solvolysis of *exo*-norborn-2-yl bromobenzene-*p*-sulfonate (**1a**) by Winstein and Trifan,[1] the reaction has been studied in finer detail stereochemically,[2] with isotopic labels,[3,4] and very extensively by considering the effect of structural modifications.[5] These developments have been to support or refute Winstein's view[1,2,6] that, whereas *endo*-norborn-2-yl brosylate (**2a**) reacts without anchimeric assistance,[7] the exo isomer **1a** ionizes with the nucleophilic assistance of the C(1)-C(6) σ bond to give the stabilized intermediate nonclassical cation **3**, which undergoes further reaction (eq 1). The conflicting interpretation that **1a** reacts without anchimeric assistance, but by a mechanism involving rapidly interconverting enantiomeric classical cations (eq 2) has been cogently expressed.[8]

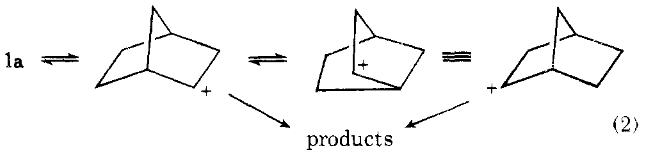


1a, R^1 = R^2 = H
b, R^1 = H; R^2 = ^{2}H
c, R^1 = ^{2}H; R^2 = H
d, R^1 = R^2 = ^{2}H



2a, R^1 = R^2 = H
b, R^1 = ^{2}H; R^2 = H
c, R^1 = R^2 = ^{2}H





Although investigations on diversely substituted norbornyl derivatives have produced many experimental results and interpretations, extrapolation to the parent has required presumptions which have not been universally accepted. Consequently, the norbornyl problem has remained controversial and is still one of the central problems of organic chemistry upon which new techniques and theories continue to be tested.[9-11]

More recently, the norbornyl cation has been generated in very acidic media at low temperatures and has been studied spectroscopically.[12] Olah and his colleagues assert that the cation has a nonclassical structure, but their interpretation of the spectra has been repudiated.[8a,13]

The structural information, however, is about a cation rendered stable by an extremely nonnucleophilic environment which is very unlike that of the intermediate in the solvolysis of **1a.** Furthermore, even if the intermediate in the solvolysis is bridged (nonclassical), the extent of bridging at the transition state for ionization is still conjectural. This question can be answered in principle by a kinetics method, but an analysis of the rates of analogues[14] is not a sufficiently subtle probe.

To the extent that the Born-Oppenheimer approximation is a good one, isotopic substitution within a molecule does not modify its potential energy hypersurface.[15a,16] Consequently, although the substitution of protium by deuterium affects the vibrational energy levels of a molecule and of its transition state for a reaction, and therefore the rate of the reaction, such substitution does not affect the mechanism of the reaction.

The use of secondary kinetic isotope effect measurements for elucidating reaction mechanisms has been reviewed.[15-17] An α-deuterium secondary kinetic isotope effect (α-kie) of ca. 1.22 (25 °C) is expected for the solvolysis of a simple secondary alkyl arenesulfonate without nucleophilic assistance.[15,17-19] This value is reduced as nucleophilic assistance increases, regardless of whether the assistance is intramolecular (neighboring group participation) or bimolecular (S$_{\mathrm{N}}$2), and in the limit is ca. 1.00.[15b,c,20] This attenuation of the α-kie has been attributed to the approaching nucleophile causing the C–H(^{2}H) vibrations in the ground state to transform into transition-state vibrations with no changes, or only compensating changes, in the magnitudes of the force constants.[15a,16a] It follows from this model that the extent of the reduction of the α-kie from ca. 1.22 (25 °C) is a (nonlinear) measure of the closeness of some atom or group to the α carbon at the transition state for the departure of the leaving group.[15c]

Shiner[15b,19] has argued that the maximal α-kie of 1.22 (25

°C) will be observed for the solvolysis of a secondary alkyl arenesulfonate only when the rate-determining step is the conversion of one type of ion pair into another. In this case the solvolytic transition state closely resembles a simple secondary carbonium ion only remotely solvated and not tightly paired with a counterion. If an unassisted ionization is rate-determining, the transition state will involve some (small) extent of covalent bonding between the nascent carbonium ion and the leaving group and this will depress the α-kie.[16a]

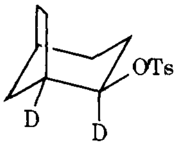
It is known that internal return is several times faster than intimate ion-pair separation in the acetolysis of **1a.**[1,6] In 80% aqueous ethanol (80E),[21] internal return is slower than further solvolysis by a factor of about 2. Consequently, if solvolysis of **1b** in both solvents is via classical cations, the α-kie in acetic acid ought to be near the known maximum (1.22, 25 °C) and the value in aqueous ethanol slightly lower. A reduction from the value of 1.22 (25 °C) for the acetolysis of **1b** would be a manifestation not only of the stabilizing involvement[22] of the electrons of the C(1)-C(6) bond in the transition state, but of bridging by the rear-side C(6) methylene.

A β-deuterium also has a rate-retarding effect upon the solvolytic substitution reaction of a simple secondary alkyl derivative.[15b,23] This β-kie is greatest for reactions which are nucleophilically unassisted and when the dihedral angle between the β-C-H(^{2}H) bond and the developing vacant orbital on the α carbon is zero.[24] This is a consequence of the stereospecific nature of hyperconjugative electron supply,[25,26] which is most effective when the β-C-H bond and the leaving group are initially trans and coplanar.[16a,27] When the β-C-H(^{2}H) bond is orthogonal to the developing vacant orbital on the α carbon, the β-kie is virtually nil.[16a,24,28]

Low α-kie values of 1.118 (CH_3CO_2H, 25 °C) and 1.124 (80E, 25 °C) have already been reported for the solvolysis of **1b** and these were interpreted as evidence for a nonclassical mechanism.[29,30] Another possibility which was considered is that the ionization is not nucleophilically assisted, but that the α-kie is low because deuterium is scrambled from C(2) in **1b** to C(1) of **1c** by internal return during solvolysis. This requires that the bridgehead β-kie for **1c** be approximately nil, which is credible in the event of a classical mechanism.[24,28] Indeed there has been a report[15c,31] that the α-kie for acetolysis of **1b** is 1.208 (25 °C) during only 3–5% of reaction (before isotopic scrambling has become extensive). A serious difficulty for this interpretation is that the α-kie measured during the whole solvolytic reaction should be distinctly lower in acetic acid than in aqueous ethanol because internal return is more extensive in the less nucleophilic solvent.[1,6,30] In fact the results[30] for the two solvents are very similar, from which it follows that the bridgehead C(1)-^{2}H and the C(2)-^{2}H have kinetic effects which cannot be too dissimilar, a prediction quite at variance with that based upon a classical mechanism.

In order to resolve these difficulties and contribute towards a more complete understanding of the mechanism of the solvolysis of *exo*-norborn-2-yl brosylate, we have prepared the mono- and dideuterated compounds **1c** and **1d** and have measured the kinetic isotope effects for their solvolyses.

The internal return concomitant with the solvolysis of racemic **1d** causes a degenerate rearrangement and consequently no scrambling of the deuterium. The kie will remain constant during the solvolysis and the two deuterium atoms should contribute multiplicatively to the cumulative effect.[15,17,25] For comparison, the kie's of two similarly dideuterated analogues, whose mechanisms were already reasonably well understood, were investigated. The dideuterated *endo*-norborn-2-yl brosylate (**2c**) has kie's of 1.191 (80E, 54.5 °C) and 1.194 (buffered acetic acid, 64.7 °C), which are in accordance with a classical mechanism.[28] The results for **2b** are 1.000 (80E, 54.5 °C) and 0.996 (buffered acetic acid, 64.7 °C), which confirm that the composite kie's are due entirely to the α-C-^{2}H.[28,30] The second model is 1,2-dideuterio-*endo*-bicyclo[3.2.1]-octan-2-yl toluene-*p*-sulfonate (**4**), which was believed on other grounds to undergo solvolysis via the nonclassical carbonium ion **5.**[32] The low composite kie's of 1.116 (80E, 64.4 °C) and 1.154 (buffered formic acid, 29.9 °C) are compatible only with a nonclassical mechanism.[33]



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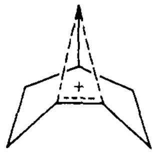


5

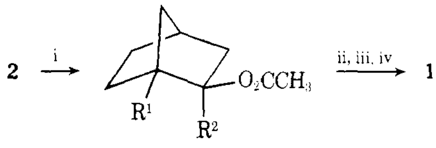
If the classical model for the solvolysis of **1** is valid, a kie of ca. 1.22 (25 °C) is anticipated for **1d.** For **1c** the *initial* kie would be ca. 1.00, but the value should increase during the solvolysis according to the extent of internal return, which scrambles the deuterium to C(2) of **1b.** Clearly, the kie ought to become significantly higher during acetolysis than during aqueous ethanolysis.

On the other hand, if the ionization involves bridging and the results of Murr and Conkling[30] are accurate, the kie for **1c** will be initially >1.00 and will increase only slightly, if at all, during the reaction. The kie of **1d** is more difficult to predict on the basis of a nonclassical mechanism. It may be expected to be less than 1.22,[33] but could be as high as 1.18 based upon the work of Murr and Conkling.[30] An isotope effect of ca. 1.22 for **1d** would therefore be ambiguous. It could be due to a classical mechanism with α-kie ≃ 1.22 and β-kie ≃ 1.00, or it could be ascribed to a nonclassical mechanism and arise from an α-kie ≃ 1.12 and a β-kie ≃ 1.09. This ambiguity should be resolved, however, by the knowledge of the kie for **1c.**

Results

Compounds **1c** and **1d** were made by standard transformations[26,30] of the specifically labeled *endo*-norborn-2-yl brosylates[28] **2b** and **2c** as illustrated in Scheme I. The deuterium contents of **2b** and **2c** were ≥99% $^2H_1$ and ≥91% $^2H_2$ and ≤9% $^2H_1$, respectively, measured mass spectrometrically; the NMR spectra together with the unambiguous synthesis established the location of the deuterium in both compounds.[28] The conversion of *endo*-norborn-2-yl brosylates into *exo*-norborn-2-yl acetates by tetra(*n*-butyl)ammonium acetate in dry benzene has been shown to occur cleanly with no scrambling of the deuterium.[30] There is no subsequent scope in the reduction of the acetates or in the brosylation of the alcohols for scrambling or loss of deuterium. The NMR spectrum of the unlabeled compound **1a** has a complex triplet at τ5.58 due to the endo hydrogen at C(2), and overlapping signals at τ7.6 and 7.7 due to the bridgehead hydrogens. The signal at τ7.6 is absent from the spectrum of **1c**,[34] and those at τ5.58 and 7.6 are absent from the spectrum of **1d.**

Scheme I



i, $(C_4H_9)_4\overset{+}{N}\overset{-}{O}_2CCH_3$/benzene
ii, $LiAlH_4$/ether
iii, $NH_4{}^+Cl^-/H_2O$
iv, $BsCl/C_5H_5N$

Rates of solvolysis in 80% aqueous ethanol and acetic acid containing 0.15 M potassium acetate were measured spectrophotometrically.[35] Rate constants and rate ratios were calculated from readings collected during ca. five half-lives and

Table I. Rate Constants and Secondary Deuterium Kinetic Isotope Effects for the Solvolysis of (**1**)[a]

	80E (25.4 °C)	CH_3CO_2H–0.15 M $K^+\bar{O}_2CCH_3$ (29.4 °C)
k^H (**1a**) × 10^3 min^{-1}	87.86 (∓0.98)	11.66 (∓0.10)
k^H (**1a**)/k^D (**1c**)	1.081 (∓0.006)[b]	1.051 (∓0.008)
	1.080 (∓0.025)[b,c,d]	1.081 (∓0.016)[c,d]
k^H (**1a**)/k^D (**1d**)	1.192 (∓0.011)	1.173 (∓0.010)

[a] Rate constants are means of six values and isotope effects are means of six ratios except where otherwise stated; errors are standard errors. Individual rate constants and standard deviations (which were normally better than 1%) were computed by a nonlinear least-squares program. [b] Rates of aqueous ethanolysis of **1a** and **1c** were measured at 25.5 °C, at which temperature $k^H = 91.45\ (\mp 1.10) \times 10^{-3}\ min^{-1}$. [c] Calculated from data obtained during the last 50% of the reaction. [d] Mean of four ratios.

also, for the solvolysis of **1a** and **1c**, from readings taken *after* one half-life had elapsed. The results are shown in Table I and are uncorrected for incomplete deuteration.

Discussion

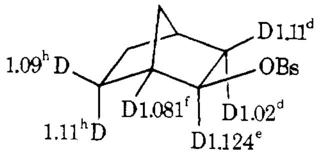
The β-kie results of 1.081 (80E, 25.5 °C) and 1.051 (CH_3CO_2H, 29.4 °C) for **1c** are significantly greater than unity and are in marked contrast to the results obtained for **2b.**[28] Moreover, the value in buffered acetic acid, in which isotopic scrambling by internal return is more extensive, is slightly *lower* than that in aqueous ethanol. The result obtained for acetolysis of **1c** during the last 50% of reaction, 1.081, shows a small upward drift as expected if the α-kie for **1b** is slightly larger than the β-kie for **1c.** The kie for **1c** in aqueous ethanol obtained from readings taken during the last 50% of reaction is identical with the result obtained during the whole reaction (though it is less precise). This is the expected result if internal return intrudes to only a small extent, as is known to be the case,[21] and especially when the α- and β-kie's are not very different, as is also now established. We conclude that, in the absence of scrambling, the α- and β-kie's are not significantly different from the results obtained during the whole reaction even in acetic acid.

The values for **1d** of 1.192 (80E, 25.4 °C) and 1.173 (CH_3CO_2H, 29.4 °C) are, within experimental error, the multiplicative results of our values for **1c** and those for **1b** reported by Murr and Conkling.[30] This suggests that the result obtained by the Jugoslav workers[15c,31] of 1.208 during only 3-5% of acetolysis of **1b** is inaccurate.

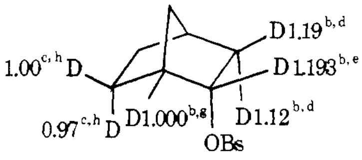
The combination of a depressed α-kie and an enhanced bridgehead β-kie is quite incompatible with the classical mechanism forthe solvolysis of **1.** The nonclassical mechanism, which is also supported by the large C(6)-γ-kie's,[21,36] satisfactorily accommodates our results.

The secondary α-, β-, and γ-deuterium kinetic isotope effect results for **1** and **2** are combined in structures **6** and **7.** The overall β-kie pattern for the endo compound shown in **7,** with nil effect at C(1)-^{2}H, a modest effect due to the *endo*-C(3)-^{2}H,[37] and a substantial effect due to the *exo*-C(3)-^{2}H,[37] is entirely compatible with a classical mechanism. In the exo isomer, the C(1)-^{2}H and *exo*-C(3)-^{2}H[37] are modestly rate retarding, but the effect of the *endo*-C(3)-^{2}H[37] is exceptionally low. This distinctive pattern shown in **6** is not easily reconciled with a classical mechanism. However, if the mechanism for the solvolysis of **1** is nonclassical and some structural modification is made which causes the mechanism to become classical, such as alkyl or aryl substitution at the *endo*-C(2) position, a predictable change in the β-kie pattern should ensue. The C(1)-^{2}H effect should decrease to approximately nil, the *endo*-C(3)-^{2}H effect should increase, and the *total* C(3)-$^2H_2$ kie should become comparable with the *total* C(3)-$^2H_2$ kie for the analogously substituted endo diastereoisomer. Insofar as the different experimental conditions allow comparisons to be made, the results[38,39] shown in **8** confirm the last of these three predictions; these results are not incompatible with a nonclassical mechanism for the solvolysis of **1,** a report to the contrary notwithstanding.[40]

Secondary deuterium kinetic isotope effects for the solvolysis of *exo*- and *endo*-norborn-2-yl brosylate

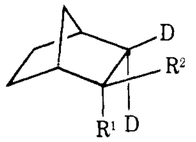


6[a]



7

a, 80% aqueous ethanol, 25 °C
b, 80% aqueous ethanol, 55 °C
c, 80% aqueous ethanol, 49 °C
d, ref 37
e, ref 30
f, present work
g, ref 28
h, ref 21



8

R¹ = CH_3; R² = OPNB, kie = 1.334
(70% aq acetone, 95 °C), ref 38
R¹ = OPNB, R² = CH_3, kie = 1.306
(70% aq acetone, 120.7 °C), ref 38
R¹ = C_6H_5, R² = OPNB, kie = 1.18
(60% aq dioxane, 39.5 °C), ref 39
R¹ = OPNB, R² = C_6H_5, kie = 1.15
(60% aq dioxane, 62.5 °C), ref 39
OPNB = *p*-nitrobenzoate

Finally, it is seen that the kie's for the solvolysis of **1d** are not as low as those for **4**[33] even after allowance has been made for temperature differences.[15b] The difference could reside in the C(1) β-kie's, or the C(2) α-kie's, or in both. However, consideration of the results for **1c,** of the dihedral angles between the C(1)-^{2}H and the C(2)-oxygen in **1d** and **4,** and of the geometry of the respective ions **3** and **5,** suggests that the difference lies largely in the α-kie's. This indicates that the rear-side bridging methylene becomes more involved with C(2) in the ionization of **4** than it does in the ionization of **1.** Since the exo- and endo-C(6) deuterium atoms exert approximately the same kinetic effect upon the solvolysis of **1**[21] the transition state for the ionization of **1,** and a fortiori that for the slower ionization of **4,**[41] must be very intermediate-like.[42] It therefore appears that the nonclassical cation **5** is more tightly bridged than **3.**

Experimental Section

The preparation and characterization of the specifically deuterated *endo*-norborn-2-yl brosylates[28] have already been described. The IR and 90-MHz NMR spectra were recorded on Perkin-Elmer Model 457 (or 577) and R32 instruments, respectively. Analytical GLC was done on Perkin-Elmer F11 chromatographs fitted with 50 ft SCOT columns (Carbowax or DEGS) using nitrogen as carrier gas.

1,2-Dideuterio-*exo*-norborn-2-yl Bromobenzene-*p*-sulfonate (1d). A solution of 1,2-dideuterio-*endo*-norborn-2-yl brosylate[28] (0.970 g; 2.91 mmol), tetra(*n*-butyl)ammonium acetate[26,30] (1.30 g; 4.90 mmol), and dry benzene (ca. 25 cm^3) was heated under reflux for 4 h. Analysis of the cooled solution by TLC showed that no norbornyl brosylate remained. The mixture was extracted between light petroleum (bp 40–60 °C) and water, and the aqueous phase was reextracted with more light petroleum. The combined organic phase was dried ($MgSO_4$), filtered, and chromatographed on deactivated alumina (100 g); the elution was with light petroleum ether. Fractions were monitored by GLC, appropriately combined, and fractionally distilled.

The residue was added to a stirred slurry of lithium aluminum hydride (0.9 g) in absolute ether (15 cm^3) and the mixture was heated under reflux for 1.5 h. The cooled reaction mixture was quenched with aqueous ammonium chloride and the mixture was then continuously extracted with ether for 20 h. The ether extract was fractionally distilled and the residue was chromatographed on deactivated alumina (60 g), the elution being with pentane–ether. Fractions were monitored by GLC, combined, and fractionally distilled. Last traces of solvent were evaporated from the residual 1,2-dideuterio-*exo*-norbornan-2-ol under reduced pressure to give a waxy solid (0.220 g; 66%). This was converted into the corresponding brosylate by the Tipson[43] procedure [0.395 g, 62%; mp (recryst, pentane) 58–59 °C; NMR τ (CCl_4) 2.34 (4 H, m), 7.71 (1 H, br s), 8.2–9.4 (8 H, m); IR $\bar{\nu}$(CCl_4) 2960, 2880, 2200 (w), 1578, 1392, 1373, 1352, 1200, 1188, 1178, 1096, 1070, 1015, 938, 928, 918, 878, and 858 cm^{-1}].

1-Deuterio-*exo*-norborn-2-yl Bromobenzene-*p*-sulfonate (1c). By reactions analogous with the ones described above, but starting from 1-deuterio-*endo*-norborn-2-yl brosylate[28] (0.600 g), 1-deuterio-*exo*-norborn-2-yl brosylate (**1c**) [0.223 g, overall 37%; mp (recryst, pentane) 59–60 °C] was obtained: NMR τ (CCl_4) 2.34 (4 H, m), 5.60 (1 H, br t), 7.72 (1 H, br s), 8.2–9.4 (8 H, m); IR $\bar{\nu}$(CCl_4) 2960, 2875, 1578, 1472, 1390, 1375, 1190, 1178, 1097, 1070, 1027, 1015, 1003, 968, 953, 938, 910, and 880 cm^{-1}.

***exo*-Norborn-2-yl Bromobenzene-*p*-sulfonate (1a).** This compound was prepared by a literature method,[3] mp (recryst, pentane) 60 °C (lit. 60 °C,[3] 55.3–57.0 °C[1]): NMR τ(CCl_4) 2.34 (4 H, m), 5.58 (1 H, br t), 7.5–7.8 (2 H, m), 8.3–9.3 (8 H, m); IR $\bar{\nu}$(CCl_4) 2970, 2880, 1578, 1390, 1375, 1350, 1190, 1178, 1098, 1070, 1063, 1015, 964, 940, 930, 916, 892, and 875 cm^{-1}.

Kinetics. The acetolysis medium was prepared by making anhydrous potassium acetate (29.44 g; 0.300 mol) and acetic anhydride (Analar grade; 20 cm^3) up to 2 l. with acetic acid (Analar grade). The 80% aqueous ethanol was made by mixing distilled water (20.0 cm^3) and spectroscopic grade absolute ethanol (80.0 cm^3).

Compound **1a** was solvolyzed simultaneously first with **1d** and then with **1c** in both solvents. The decrease in the absorbance of each solution at 276.5 nm was monitored automatically in the thermostatted cell compartment of a Unicam SP500 Series 2 ultraviolet spectrophotometer fitted with an SP505 program controller coupled to an SP22 recorder. The temperature stability was shown to be better than $\mp$ 0.01 °C, though the actual temperatures quoted are accurate to only ca. $\mp$ 0.1 °C.

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