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Solvolysis of Haloallenes. The Effect of Added Salts on the Polarimetric and Titrimetric Rates of Solvolysis of 1-Bromo-3-methyl-1,2-pentadiene

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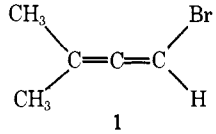
Abstract: The effect of added LiCl, LiBr, $LiClO_4$, and NaN_3 and the effect of solvent nucleophilicity on the polarimetric and titrimetric rates of solvolysis of (*R*)-(−)-1-bromo-3-methyl-1,2-pentadiene and its racemic modification are reported. The data are reconciled with a mechanism of solvolysis involving nucleophilic attack on a tight ion pair. Marked increases in k_{rac} with added Br^- in 97:3 (w/w) 2,2,2-trifluoroethanol–water and with added N_3^- in 60:40 (v/v) ethanol–water and $k_{rac} \neq 0$ in the absence of added nucleophile are key elements in this interpretation. Internal return with rearrangement is also discussed.

The previous paper in this series[2] reported the effect of changing solvent nucleophilicity on the rate of solvolysis of a variety of di- and trisubstituted haloallenes. In general these compounds exhibited behavior typical of saturated halides undergoing solvolysis by a limiting mechanism but with notable exceptions.[3] Typical of these exceptions is the behavior of **1**



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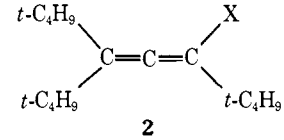
which yields $m = 0.88$ vs. Y in aqueous ethanol, $(k_H/k_D)_\alpha = 1.20$ in 50E,[4] 1.23 in 70T,[4] and 1.28 in 97T,[4] and $(k_H/k_{CD_3})_\beta = 1.33$ in 50E, 60E,[4] 70T, and 97T. Interestingly, however, the $(T/E)_Y$[5] rate ratio exhibited by **1** is 0.63. We concluded that while the former data might imply solvolysis via a limiting mechanism, the lower rate of solvolysis in the nonnucleophilic solvent at constant Y was more consistent with the behavior of saturated substrates undergoing solvolysis with considerable assistance by solvent attack on neutral substrate or ion pair.[3b,6] Nor is the phenomenon unique to **1**. In fact, the 70T/50E rate ratio diminishes along the series $(t\text{-}C_4H_9)_2C{=}C{=}C(H)Br > t\text{-}C_4H_9(CH_3)C{=}C{=}C(H)Br > (CH_3)_2C{=}C{=}C(H)Br$, being 8.2, 3.7, and 1.8 respectively.[2] In addition **2** (X = Cl)



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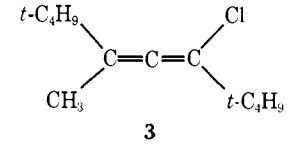

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exhibits a 97T/60E rate ratio of 900 while **3** reacts only 12 times as rapidly in this nonnucleophilic solvent.[2] These data thus imply the possibility of an increasingly important component of nucleophilic solvent assistance as steric hindrance is removed. Indeed the relatively low CH_3/H ratio, **1**/**4** = $10^{4.3}$ in 80E at 25 °C, provides some support for this contention, particularly when one notes that the $t\text{-}C_4H_9/H$ ratio **2** (X = Br)/**5** = $10^{3.1}$. It might be expected that the greater electron-releasing effect of the *tert*-butyl group would result in a larger ratio than is observed for methyl substitution. Impor-

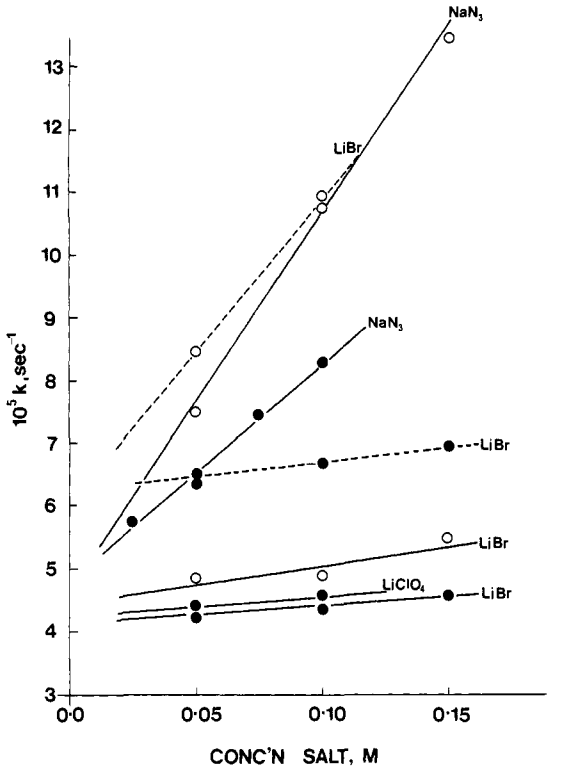
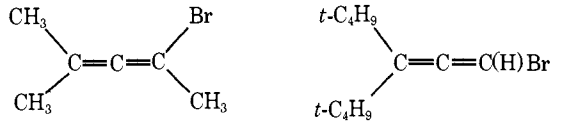


Figure 1. Experimental data for solvolysis of 1-bromo-3-methyl-1,2-pentadiene: ●, titrimetric rates; ○, polarimetric rates; solid lines, 60E; dashed lines, 97T.



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tantly the ratio **2** (X = Br)/**5** increases to $\geq 10^{5.1}$ in 97T, implying a degree of solvent assistance present in the solvolysis of **5** in aqueous ethanol not found in **2** (X = Br). Finally, it must be noted that disubstituted bromoallenes like **1** are about as reactive as secondary carbinyl bromides, $k_1/k_{i\text{-PrBr}} = 1.4$, which have been shown to solvolyze with substantial assistance by solvent.[3b,7]

For these reasons it seemed important to examine the detailed mechanism of solvolysis of a relatively unhindered disubstituted bromoallene to ascertain whether the solvolysis reactions of these compounds are properly classed as borderline and whether solvent assistance of some type is indeed involved as well as the point of its intervention in the mechanistic scheme.

We chose to exploit the possibility of dissymmetry in the allene moiety thereby allowing the measurement of polarimetric as well as titrimetric rates of solvolysis. We assumed that this classic test for the incursion of ion pairs in solvolysis reactions would at the very least provide the first conclusive evidence regarding their involvement, or lack of it, in the solvolysis of haloallenes, a point hitherto unsubstantiated.[8] At best we anticipated that changes in k_α and k_t with [Nu^-] and with solvent nucleophilicity would provide the detailed answers we were seeking regarding the degree and point of solvent assistance.

(*R*)-(−)-1-Bromo-3-methyl-1,2-pentadiene (**6**) and its racemic modification were chosen for study because of their obvious similarity to **1** and the fact that they are the simplest 3,3-disubstituted bromoallenes capable of resolution into optical antipodes.[9,10]

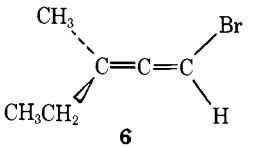

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Table I. Polarimetric and Titrimetric Rates of Solvolysis of 1-Bromo-3-methyl-1,2-pentadiene (**6**) at 54.5 ± 0.03 °C

Solvent	Salt	10^5k, s^{-1} [a]	Method
60E	None	4.10 ± 0.04	T[b]
		4.65 ± 0.09	P[c]
	0.050 M LiCl	4.29 ± 0.20	T
	0.100 M LiCl	4.24 ± 0.17	T
	0.150 M LiCl	4.24 ± 0.11	T
	0.050 M LiBr	4.28 ± 0.05	T
		4.83 ± 0.13	P
	0.100 M LiBr	4.42 ± 0.07	T
		4.90 ± 0.06	P
	0.150 M LiBr	4.55 ± 0.05	T
		5.50 ± 0.02	P
	0.050 M $LiClO_4$	4.38 ± 0.09	T
		4.59 ± 0.02	P
	0.100 M $LiClO_4$	4.52 ± 0.11	T
		4.96 ± 0.05	P
	0.150 M $LiClO_4$	5.26 ± 0.10	P
	0.0250 M NaN_3	5.73 ± 0.04	T
	0.050 M NaN_3	6.41 ± 0.24	T
		7.49 ± 0.22	P
	0.075 M NaN_3	7.45 ± 0.01	T
	0.100 M NaN_3	8.29 ± 0.03	T
		10.8 ± 0.3	P
	0.150 M NaN_3	13.5 ± 0.10	P
97T[d]	None	5.78 ± 0.11	T
		6.18 ± 0.09	P
	0.050 M LiBr	6.43 ± 0.01	T
		8.46 ± 0.13	P
	0.100 M LiBr	6.69 ± 0.16	T
		10.9 ± 0.3	P
	0.150 M LiBr	6.96 ± 0.16	T
	0.050 M LiCl	6.99 ± 0.05	T
	0.100 M LiCl	6.87 ± 0.04	T

[a] Average deviation of duplicate or triplicate determinations. [b] Titrimetric, substrate concentration 6–8 × 10^{-4} M. [c] Polarimetric, substrate concentration 4–6 × 10^{-3} M. [d] Substrate and/or salt solubility precluded studies with added N_3^- or ClO_4^- in this medium.

Results

Table I presents the results of our investigation. Figure 1 displays these results in a form useful for further discussion. Tables II and III present derived data as indicated. Both polarimetric and titrimetric rates exhibited pseudo-first-order behavior to more than 85% reaction. Titrimetric and polarimetric information was obtained from solutions of nearly identical concentrations, 6 × 10^{-4} to 6 × 10^{-3} M in substrate. This was possible because of the use of an autobalancing polarimeter capable of providing rotations to the nearest 0.2 mdeg and the use of a micro pH-stat titrating system capable of providing volumetric data to the nearest 0.002 mL. Each instrument provided digital output to a microprocessor interfaced with a digital clock as well. This allowed several hundred data points to be acquired for each run.

Product isolation studies in this system give no useful information regarding mechanism for five reasons.

(1) Previous work has shown that propargyl alcohols are the major products isolated, usually in >90% yield; some unsaturated carbonyl compounds are found in cases where steric hindrance at C-3 makes attack at C-1 more competitive.[11]

(2) If allenyl ethers are formed, as also might be expected, they are known to be relatively unstable under mildly acidic conditions yielding primarily α,β-unsaturated carbonyl compounds.[12]

Table II. Winstein b Values[a] for Solvolysis of **6**

	60E		97T	
Salt	k_α	k_t	k_α	k_t
LiCl		0		0
$LiClO_4$	0	0.8		
LiBr	1.4	0.7	8.1	0.8
NaN_3	9.5	7.4		

[a] Calculated in the usual manner from $k = k_0(1 + b[\text{salt}])$.

(3) The propargyl alcohols formed in these solvolyses undergo partial rearrangement at the temperatures used here (Meyer-Schuster) to α,β-unsaturated carbonyl compounds particularly in the later stages of the reaction.[13]

(4) Allenyl and propargyl azides are known to be unstable to the reaction conditions;[14] experimental and calculated infinity titers agreed to ±1.2% in all titrimetric rate constants measured including those in the presence of N_3^-.

(5) Attack by nucleophile or solvent at C-1 (allene terminus) leads either to a product unstable to the reaction conditions as described above or to one incapable of exhibiting optical activity; attack at C-3 (propargyl terminus) can occur theoretically at either enantiotopic face of the allene moiety with equal facility, thus leading to racemic products. Measured infinity rotations in all polarimetric studies were 0 ± 2 mdeg. Initial rotations in the kinetic solutions were 180–240 mdeg.

Discussion

Several features of the solvolysis reaction are apparent from the data in Tables I–III and Figure 1.

(1) The ratio k_α/k_t[15] remains constant with changing solvent nucleophilicity, being 1.13 ± 0.04 in 60E and 1.07 ± 0.04 in 97T in the absence of added salts; $10^5k_{rac}{}^{60E} = 0.55$, $10^5k_{rac}{}^{97T} = 0.43$.

(2) No common ion effect is observed experimentally.

(3) No special salt effect is observed experimentally with $LiClO_4$ in 60E; variations of experimentally measured values of k_α and k_t in the absence of added salts and those extrapolated are within experimental error. Azide ion is apparently an exception as discussed below (ref 18).

(4) k_t exhibits a shallow linear dependence on $[Cl^-]$, $[ClO_4^-]$, and $[Br^-]$ in 60E and on $[Cl^-]$ and $[Br^-]$ in 97T (Figure 1 and Table II).

(5) k_α exhibits a dependence on $[ClO_4^-]$ and $[Br^-]$ in 60E similar to that of k_t.

(6) k_α and k_t show marked enhancement upon addition of N_3^- in 60E, the dependence of k_α being somewhat steeper (b = 9.5 vs. 7.4 for k_t). The dependence of k_α and k_t when corrected for the normal salt effect indicated in Table II yields $k_\alpha \propto [N_3^-]^{0.31}$ and $k_t \propto [N_3^-]^{0.28}$. Thus k_{rac} increases from 0.55 in absence of salt to 2.37 in 0.100 M NaN_3.

(7) k_α also shows substantial enhancement upon addition of LiBr in 97T: k_t does not, i.e., k_{rac} increases markedly with increasing $[Br^-]$ being 0.43 in the absence of salt and 4.1 at $[Br^-] = 0.100$ M. In 60E k_{rac} is constant.

We contend that the results presented are consistent with a mechanism of solvolysis involving attack by added nucleophile or solvent on a configurationally stable species.[16] The results in 97T require such a mechanism to be operative in the presence of added Br^-. In this solvent, k_α is markedly increased by added Br^- while k_t shows only a normal linear salt effect. We interpret this to require Br^- to be capturing a species which normally retains configuration upon return to its immediate precursor. That is, Br^- competes favorably with the nonnucleophilic solvent TFE for an ion pair effectively reducing return to covalent R-Br of *retained* configuration but resulting rather in return to racemized R-Br or R′Br (see below) without enhancement of the solvolysis rate, k_t (Figure 2). The most likely species involved here is the intimate ion pair, I (Figure 2). If this is the case then it might be expected that Br^- would not compete as favorably with a more nucleophilic solvent such as 60E.[17] Indeed k_t and k_α show a nearly identical response to added LiBr in 60E; k_{rac} remains constant.

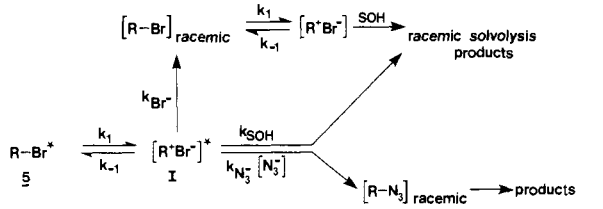


Figure 2. Solvolysis scheme for reactions of 1-bromo-3-methyl-1,2-pentadiene.

Table III. Rate Constants for Racemization, k_{rac}, of (*R*)-(−)-1-Bromo-3-methyl-1,2-pentadiene in 60E and 97T at 54.5 °C

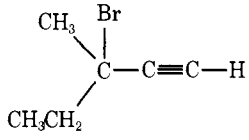
	10^5k_{rac}, s^{-1}		
	60E		97T
[Salt], M	N_3^-	Br^-	Br^-
None	0.55	0.31	0.43
0.050	1.09	0.47	1.96
0.100	2.37	0.64	4.10

The addition of N_3^- to the solvolysis medium (60E) has quite a different effect. Here k_{rac} increases with $[N_3^-]$ even though k_t is accelerated beyond the value expected from a normal salt effect. This result can be considered indicative of attack by N_3^- on an ion pair which retains configuration if it is noted that the species formed upon reaction with N_3^-, R-N_3, is known to be quite unstable to the reaction conditions. Thus the enhancement observed in k_t most likely arises from incursion of a new and more facile pathway to products while the enhancement in k_α arises from suppression of internal return. Specifically, decomposition of R-N_3 must occur faster than its possible return to intimate ion pair I (Figure 2).[18] Such an increase in k_t is not observed in 97T upon addition of Br^- because internal return and nucleophilic attack by Br^- on I are degenerate processes with regard to k_t but not k_α.

Any mechanistic scheme involving classical S_N2 attack by solvent or Nu^- is ruled out by $k_{rac} \neq 0$ and by the wealth of inconsistent mechanistic data cited in the introduction. Also ruled out is a mechanism similar to that suggested by Bordwell,[3d] i.e., the ion-pair sandwich mechanism, since involvement of the nucleophile in formation of the solvated ion sandwich cannot account for $k_{rac} \neq 0$ at *all* salt concentrations. Also it is unlikely that a special salt effect has gone undetected here and that the solvent separated ion pair is the species being captured by azide in 60E since it might be expected that racemization occurs during its formation and return and therefore total capture of that species should lead to $k_t \rightarrow k_\alpha$ or $k_{rac} \rightarrow 0$ with increasing $[N_3^-]$.[15] However, we are exploring the possibility of mechanistic schemes involving only partial racemization in external ion pair return through a study of ^{18}O equilibration and exchange vs. k_{rac} in allenyl 3,5-dinitrobenzoates.

Question of Internal Return with Rearrangement. It has been implicitly assumed in these discussions that nucleophilic attack on ion pair I may occur at C-1 (allenyl terminus) or C-3 (propargyl terminus). Either event leads to the formation of racemic products as described earlier; at C-1 due to tautomerism, at C-3 due to attack with equal facility at either enantiotropic face. In the latter case it must be assumed that the

counterion of the tight ion pair is sufficiently remote from C-3 as to exercise minimal influence on the stereochemistry of reaction at that site. The question of internal return from I with rearrangement to propargyl bromide (**6**) cannot be answered



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from the data presented here. Indeed, **6** is expected to react much faster (ca. 40 times) than **5** and as such would be kinetically undetectable. Obviously, this bears on the question of the relationship between the structure(s) of ion pairs derived from propargyl halide solvolysis and those observed here.[19] A study of salt effects in the solvolysis of a variety of isomeric propargyl derivatives is in progress.

Experimental Section

Infrared spectra were obtained using a Perkin-Elmer Model 337 infrared spectrophotometer. Preparative gas–liquid chromatography was performed on a Hewlett-Packard chromatograph, Model 5750. ^{1}H NMR spectra were obtained on an Hitachi Perkin-Elmer R-20B nuclear magnetic resonance spectrometer, 60 MHz.

Materials. 2,2,2-Trifluoroethanol (Halocarbon Products) was purified according to Shiner et al.[20] or Rappoport.[21] Ethanol was purified in 3-L batches by distillation of commercial absolute ethanol from diethyl phthalate to which a small amount of Na^0 had been added. (±)-3-Methyl-1-pentyn-3-ol (Aldrich) was distilled prior to use. (*S*)-(+)-3-methyl-1-pentyn-3-ol was obtained from the racemic alcohol by the method of Hickman and Kenyon.[9] Triethylamine proved more effective than pyridine in the preparation of the half phthalate ester. Six recrystallizations of the brucine salt were required. All salts used were anhydrous reagent grade or primary standard (B and A or G. Frederick Smith).

1-Bromo-3-methylpentadiene was prepared according to the method of Landor.[22]

***(R)*-(−)-1-Bromo-3-methylpenta-1,2-diene** was prepared according to the procedure of Landor.[10,22] From an analysis of the stereospecificity of the reaction as indicated by Landor[10] and knowledge of the absolute configuration of the starting alcohol[9] we conclude that (*S*)-(+)-3-methyl-1-pentyn-3-ol yields (*R*)-(−)-1-bromo-3-methylpenta-1,2-diene. Rotations on the neat liquid at 25 °C in a 1-dm cell were −30.5 and −60.2° at 578 and 365 nm, respectively.

Kinetic Studies. Polarimetric rate constants were measured on a Perkin-Elmer Model 241 digital polarimeter at 365 nm, using a 1-mL capacity, 1 dm, quartz window, thermostated microcell. The polarimeter and a Chronolog Model 32001 digital clock were interfaced with a Wang Model 600 advanced programmable calculator programmed for the acquisition of data on magnetic tape. Up to 200 points were normally recorded. A small sample of the optically active bromoallene was purified by preparative GC (10 ft × 0.5 in., SE-30, 110 °C) immediately prior to use and 2.0–2.5 μL (preweighed syringe) was dissolved in 2 mL of the appropriate solvent. After dissolution of the substrate (ca. 30–40 s) the cell was filled and allowed to thermostat for 10 min (ca. 3 min was found to be the actual time necessary for complete equilibration) before the data recording began. Initial rotations under these conditions were −0.180 to −0.240° higher than the values observed in 97% TFE. All polarimetric runs were done in duplicate and some in triplicate.

Titrimetric rate constants were measured using a Radiometer pH-stat titrator consisting of a Model ABU 13 2.5-mL capacity automatic buret with digital output and TTT 60 titrator controller interfaced as above. To initiate a run, 3.0–3.5 μL (preweighed syringe) of purified (preparative GC) bromoallene was injected into 15 or 20 mL of the appropriate solvent previously thermostated for 20 min in the sealed titrimetric cell. The mixture was continually stirred during the course of the run. Early work indicated a pH-dependent, metal-catalyzed component in the titrimetric rate constant. This was traced to a stainless steel shaft in the mechanical stirrer utilized. Substitution of a Teflon stirrer remedied this problem. All titrimetric runs were accomplished in duplicate or triplicate with approximately 150 points collected per run. Sample sizes were such as to effect infinity titers of standard NaOH prepared in the appropriate solvent plus salt of ca. 1.8 mL read with a precision of ±0.002 mL. The effect of dilution was not noticeable up to 85% reaction.

Temperature control and measurement were accomplished using a PRT regulated proportional temperature controller and Hewlett-Packard quartz thermometer. Calculation of rate constants was accomplished using a nonlinear exponential fit least-squares program written by DeTar[23] and modified by us.

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References and Notes

(1) On leave 1976–1977, Department of Chemistry, University of Aberdeen, Scotland, to whom the senior author is indebted for the use of facilities and gracious hospitality.
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(3) Excellent reviews on the classification of solvolysis reactions as borderline and/or limiting and a detailed analysis of the involvement of ion pairs and nucleophilic solvent assistance are available. See, for example, (a) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973); (b) J. M. Harris, *Prog. Phys. Org. Chem.*, **11**, 89 (1974); (c) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley, New York, N.Y., 1974, Chapter 3; (d) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 133 (1975), and immediately preceding papers.
(4) 50E = 50:50 (v/v) ethanol–water; 60E = 60:40 (v/v) ethanol–water; 70T = 70:30 (w/w) 2,2,2-trifluoroethanol–water; 97T = 97:3 (w/w) 2,2,2-trifluoroethanol–water.
(5) 2,2,2-Trifluoroethanol:ethanol rate ratio at constant *Y*; the value reported assumes $Y_{97T} = Y_{60E} = 1.12$. If $Y_{97T} = 0.93$ as defined by adamantyl tosylate solvolysis, $(T/E)_Y = 0.91$.
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(15) k_α = polarimetric rate constant as usually defined; k_t = titrimetric rate constant as usually defined; $k_{rac} = k_\alpha - k_t$; see S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965).
(16) It should be noted here that 1,3,3-triphenyl-1-chloropropadiene exhibits a common ion rate depression of 29% in 0.10 M LiCl in aqueous acetone, thus implicating dissociated ions in its solvolysis.[11a]
(17) Specifically, in 60E $(k_{SOH}/k_{-1}) > (k_{Br^-}/k_{-1})$.
(18) Further support of this interpretation is gained from examination of the extrapolated value of the titrimetric rate constant. If the data from added N_3^- are used k_t(extrapolated) = k_α(extrapolated) = k_α(no salt, experimental). It must be noted that all other salts in 60E give values of k_t(extrapolated) approximately equal to k_t(no salt, experimental). This fact implies that capture of the tight ion pair is complete and return to I does not occur. The same phenomenon is noted with added Br^- in 97% TFE. Note added in Proof: Alternatively, the increase in k_t with added N_3^- may be due to a special salt effect between the two linear ions, N_3^- and $R_2C{=}C{=}CH^+$.
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