we must be cautious in calculating the amount of common ion return kinetically, because small high charge density anions, such as hydroxide and fluoride, can retard reaction, and estimation of any rate enhancing effect of the common ion is fraught with uncertainty.[58] Use of an isotopically labeled common ion is also not the answer, because it could exchange with the leaving anion at the ion pair stage.[17]

Although we conclude that interactions between an anion and a carbonium-ion-like transition state are important factors in determining kinetic salt orders in polar hydroxylic solvents, other factors including the conventional ionic atmosphere effects and dipole-dipole effects undoubtedly contribute to the overall effect.[18] The relation between rate constant and salt concentration also suggests that more than one factor is at work.

Except for the treatment used by Perrin and Pressing,[18] most of the electrostatic treatments of kinetic salt effects predict a linear relation between log k and ionic strength (or its square root for interionic reactions).[3,35] However, Winstein and his coworkers found that kinetic salt effects in many nonpolar solvents

(58) The small rate retardations observed with fluoride or acetate ions could in principle be caused by return of a reaction intermediate to an unreactive alkyl fluoride or acetate.

were linear with ionic strength,[17a] as would be expected if there were direct 1:1 interactions between say a lithium cation and the anionic leaving group (*cf.* ref 13).

As we noted earlier our results fit neither a linear nor a logarithmic relationship between rate and ionic strength, although for many electrolytes k varies linearly with ionic strength up to moderate salt concentrations and then increases more sharply.

That part of the salt effect which involves solvent-structure-induced (hydrophobic) ion pairing could very well lead to linear relations between rate and ionic strength, whereas those caused by ionic atmosphere effects[3] and by salt effects upon the activity coefficient of the substrate[7] should follow a logarithmic relationship. Insofar as all the effects contribute to the overall effect it is not surprising that the relation between rate and ionic strength is in between linear and logarithmic.

Reactions of 2-Halo-2,3,3-trimethylbutanes in Methanol Solution. Rates and Product Ratios in Solvolysis and in Reactions with Anionic Bases[1]

J. F. Bunnett* and David L. Eck

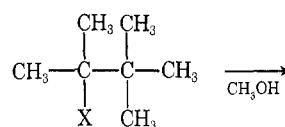*University of California, Santa Cruz, California 95060*

Received August 24, 1970

Reactions of 2-chloro-2,3,3-trimethylbutane (1a) in CH_3OH to form 2,3,3-trimethyl-1-butene (2) and 2,3,3-trimethyl-2-butyl methyl ether (3) are accelerated by added electrolytes in the order $NaClO_4$ > $NaSC_2H_5$ > $NaOCH_3$. The kinetic effects of $NaClO_4$ plus $NaOCH_3$ or $NaSC_2H_5$ are not additive. Low concentrations of $NaOCH_3$ cause a small rate increase but larger concentrations cause the rate to diminish. $NaClO_4$ does not affect the proportions of 2 and 3 formed from 1a, but $NaOCH_3$ and especially $NaSC_2H_5$ cause an increase in the fraction of olefin in the products. 1a and its bromo and iodo analogs differ, in solvolysis and in reactions with $NaOCH_3$ or $NaSC_2H_5$, in the proportions of 2 and 3 formed. The data suggest reaction in part by E1–Sn1 solvolysis and in part by the E2 mechanism, but no model to give a satisfactory quantitative account of the data has been found.
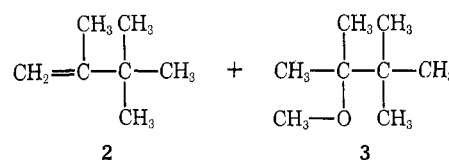
Part A

Much scientific interpretation consists of the fitting of experimental data to conceptual models, often with demonstration that certain models can and that other models cannot accommodate the data. Sometimes new models are devised *ad hoc* when none of the older ones seems adequate. However, there are occasions when experimental data outrun the supply of models; we now present data of this character.

These data concern principally rate and product studies on the solvolysis of 2-chloro-2,3,3-trimethylbutane (1a) in methanol, both in the absence and in the presence of sodium perchlorate, and on its reactions with sodium methoxide and sodium thioethoxide. For reactions of the bromo and iodo analogs of 1a, we have studied only product compositions, except for a short series of kinetic data on the iodo compound, presented in Part B. The products obtained from all reactions are an olefin, 2,3,3-trimethyl-1-butene (2), and an ether, 2,3,3-trimethyl-2-butyl methyl ether (3). No dialkyl sulfide product was detectable in the sodium thioethoxide reactions. Our original purpose was to compare CH_3O^- and $C_2H_5S^-$ as to their effectiveness in bringing about E2 elimination

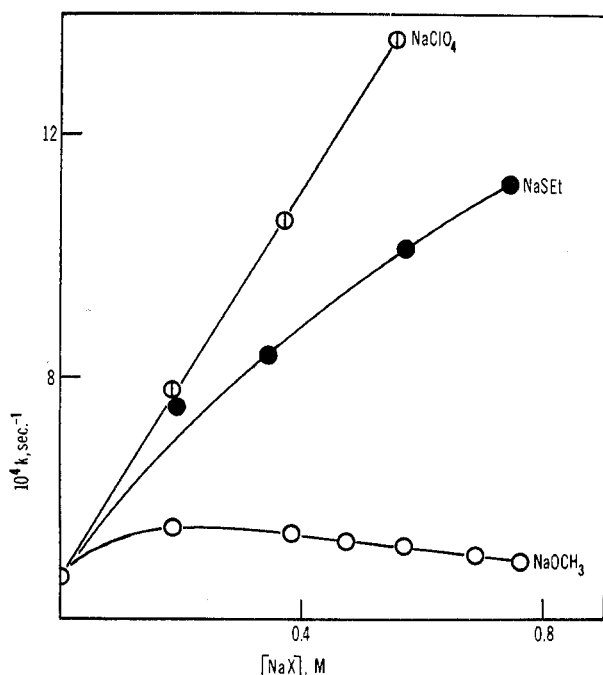1a, X = Cl
b, X = Br
c, X = I

2

3

Figure 1.—Pseudo-first-order rate coefficients for reaction of 2-chloro-2,3,3-trimethylbutane (1a) with various sodium salts at several concentrations in methanol at 69.9°: open circles, solvolysis or NaOCH₃; filled circles, NaSC₂H₅; barred circles, NaClO₄.

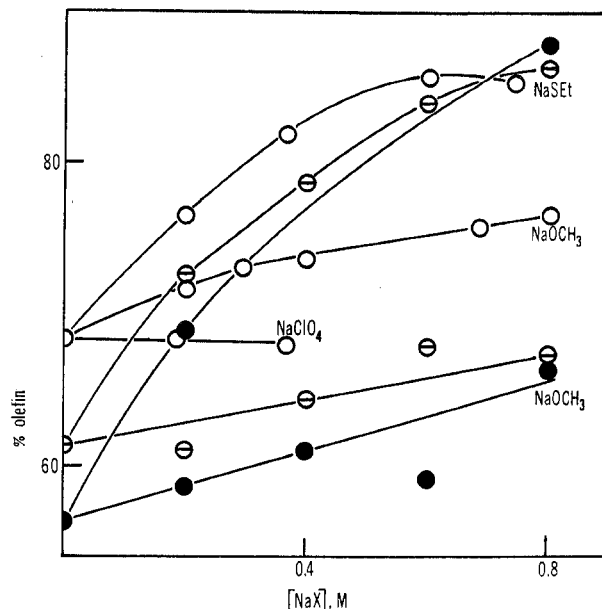Figure 2.—Per cent of olefin 2 formed from 1a, 1b, and 1c in solvolysis and in reaction with NaOCH₃ or NaSC₂H₅, and from solvolysis of 1a in the presence of NaClO₄: open circles, chloride 1a; barred circles, bromide 1b; filled circles, iodide 1c. The sodium salts involved are designated at the right.

to **2**, but the data turn out to be only marginally useful for that purpose.

All reactions were conducted with the base in large excess over the substrate, and clean pseudo-first-order kinetics were observed. In solvolysis reaction mixtures, 2,6-lutidine was included to neutralize the hydrogen halide by-product; both in a previous study[2] and in the present work it was shown that the inclusion of 2,6-lutidine affects neither rates nor product compositions. Rates were followed by argentimetric titration of halide ion. Products were determined by glpc. There was no evidence for any product other than **2** and **3**, and the absolute yields of **2** and **3** when occasionally checked against an internal standard totaled 100%.

In Figure 1, many of our kinetic data are displayed. It is noteworthy that NaOCH₃ had but a modest effect on overall reaction rate: a slight increase up to about 0.2 M NaOCH₃, and then a gentle and nearly linear decrease. The kinetic effect of the mercaptide base was considerably greater; 0.75 M NaSC₂H₅ caused the rate to more than double.[3] The kinetic response shows a gentle downward curvature. Sodium perchlorate had the strongest kinetic effect; 0.55 M NaClO₄ caused an approximate tripling of solvolysis rate, the response being strictly linear.

The effects of these sodium salts on the product composition from all three alkyl halides (1a, 1b, and 1c) are shown, as per cent olefin (2), in Figure 2.

Further sets of experiments involved constant concentrations of either NaOCH₃ or NaSC₂H₅ and variable concentrations of NaClO₄, with determination both

of rates and product compositions. Results are set forth in Table I.

TABLE I
REACTIONS OF 2-CHLORO-2,3,3-TRIMETHYLBUTANE (1a)
WITH NaOCH₃ OR NaSC₂H₅ IN THE PRESENCE
OF NaClO₄ IN METHANOL AT 69.9°

Base	[Base],[a] M	[NaClO₄],[a] M	$10^4 k\psi$, sec⁻¹	Yields, % — 2	3
NaOCH₃	0.802		(4.93)[b]	76.6	23.4
	0.802	0.184	6.69	75.8	24.2
	0.802	0.368	7.94	74.8	25.2
	0.802	0.552	10.37	73.7	26.3
	0.802	0.736		72.9	27.1
NaSC₂H₅	0.368[c]		(8.58)[b]	81.8	18.2
	0.368[c]	0.184	11.10	80.1	19.9
	0.368[c]	0.368	13.98	78.4	21.6
	0.368[c]	0.552	16.36	77.1	22.9
	0.368[c]	0.736		75.8	24.2

[a] Concentrations are corrected for solvent expansion. [b] Interpolated or extrapolated in Figure 1. [c] C₂H₅SH, 0.184 M, also present.

Discussion

A leaving group effect on solvolysis products is evident in Figure 2: the more basic the leaving group, the greater the fraction of olefin that is formed. This is a further example of an effect noted by Cocivera and Winstein.[4] It is attributed to reaction within the initial intimate ion pair; the anion, if basic, can take a proton from the carbonium ion, forming some olefin before the two ions become separated by solvent.

Although NaClO₄ greatly affects solvolysis rate, it does not affect the product ratio (see Figure 2). This was also observed in a previous study involving benzyl-dimethylcarbinyl chloride.[2] This implies that the kinetic effect of NaClO₄ does not involve either transformation of R⁺Cl⁻ to R⁺ClO₄⁻ intimate ion pairs or alteration of the extents to which products are

(2) J. F. Bunnett, G. T. Davis, and H. Tanida, J. Amer. Chem. Soc., 84, 1606 (1962).

(3) Ethanethiol, usually at about half the concentration of NaSC₂H₅, was present in all reactions involving the mercaptide base.

(4) M. Cocivera and S. Winstein, J. Amer. Chem. Soc., 85, 1702 (1963).

formed from R^+Cl^- intimate ion pairs and from solvent-separated ions. This implication is based on assumptions that the proportions of products **2** and **3** from R^+X^- intimate ion pairs would differ when X^- was chloride or perchlorate, just as they do when X^- is chloride, bromide, or iodide, and that the product proportions from R^+Cl^- intimate ion pairs and from solvent-separated ions would differ. It therefore seems necessary to assign $NaClO_4$ the role of accelerating, through a salt effect, the initial ionization to intimate ion pairs.

We have sought to fit our data to various conceptual models for this system, but we have been unable to find a model which gives a satisfactory quantitative account of both the kinetic and product data. One model that was tried was a combination of E1-SN1 solvolysis, subject to linear acceleration or deceleration by the various salts present, and an E2 component not subject to salt effects. Another was similar, except that it allowed for the possibility that a negative salt effect by $NaOCH_3$ might be superimposed on a positive salt effect by $NaClO_4$. As discussed in Part B, neither of these models was satisfactory.

No doubt it would be possible to fit our data to a model having a large number of adjustable parameters. Conceivably the chemical situation requires such a complex model. We have not pursued this approach because of the difficulty of verifying such a model, even if it does accommodate the data.

The possibility that there is no E2 component in these systems has been considered, and is disfavored for reasons we shall now discuss. In this model, products would be formed exclusively from ion pair or free carbonium ion intermediates. The model is disfavored on considerations of analogy, and because of the fact that olefin yield in the presence of $NaOCH_3$ or $NaSC_2H_5$ depends on $NaClO_4$ concentration (Table I).

In the analogous system of benzyldimethylcarbinyl chlorides, both hydrogen isotope effects[2] and Hammett ρ parameters[5] call for an E2 component.[6] Qualitatively, many phenomena in that system resemble observations made in the present study. An E2 component is therefore probable in the present system.

Inasmuch as $NaClO_4$ is judged not to affect the relative amounts of product formation from intimate ion pairs and from free ions in the absence of $NaOCH_3$ and $NaSC_2H_5$, it is unlikely to affect the relative amounts of olefin and ether formed from intimate ion pairs or free ions in the presence of these bases. Therefore, without an E2 component, the yield of olefin in the presence of $NaOCH_3$ or $NaSC_2H_5$ should not depend on the concentration of $NaClO_4$. However, the yield of olefin does depend on $NaClO_4$ concentration, both in 0.8 M $NaOCH_3$ and in 0.37 M $NaSC_2H_5$ (Table I). It follows that the reaction involves an E2 component.

Experimental support for this reasoning is provided by a recent study of the reaction of 2,2,2-triphenylethyl tosylate with $NaOCH_3$–CH_3OH, which forms 1,1,2-triphenylethene and 1,1,2-triphenylethyl methyl ether; the product ratio with 0.85 M $NaOCH_3$ is unaffected by $NaClO_4$ in concentrations as high as 0.6 M.[7] Both products have rearranged carbon skeletons, and it is unlikely that recombination of tosylate ion with the 1,1,2-triphenylethyl cation occurred after rearrangement. There was almost certainly no E2 component; the lack of effect of $NaClO_4$ on products supports our reasoning above.

On the other hand, $NaClO_4$ does affect the ratio of camphene to camphene hydrate methyl ether from reaction of isobornyl chloride or camphene hydrochloride with $NaOCH_3$ in CH_3OH.[8] Here also an E2 component is unlikely. Therefore our conclusion that the reactions of **1a** with $NaOCH_3$ and $NaSC_2H_5$ involve an E2 component can only be advanced with some qualification.

Part B

Experimental Section

Materials. 2-Chloro-2,3,3-trimethylbutane (**1a**), from Aldrich Chemical Co., was purified by the method of Calingaert, *et al.*[9] The corresponding bromide (**1b**) and iodide (**1c**) were made by reaction of 2,3,3-trimethyl-2-butanol[9] with aqueous HBr and HI, respectively. All three halides had physical properties in agreement with those recorded in the literature;[9-11] for each, the nmr spectrum comprised the expected two singlets, in relative areas 3:2. **2,3,3-Trimethyl-1-butene** (**2**) was obtained by sulfuric acid catalyzed dehydration of 2,3,3-trimethyl-2-butanol; its boiling point (78°) is consistent with the literature;[12] its purity was >99% as judged by glpc; δ^{CCl_4} 1.05 (s, 9) *tert*-C_4H_9, 1.70–1.73 (m, 3) CH_3, 4.53–4.68 (m, 2) vinyl CH_2.

Methyl 2,3,3-Trimethyl-2-butyl Ether (3).—To a stirred suspension of 0.12 g (0.06 mol) of NaH in 10 ml of dimethyl sulfoxide (DMSO) was added dropwise a solution of 3.48 g (0.03 mol) of 2,3,3-trimethyl-2-butanol in 15 ml of DMSO. The mixture was stirred overnight at 40–50°, a solution of 5.68 g (0.04 mol) of CH_3I in 10 ml of DMSO was added, and stirring was continued for 24 hr. Pentane (20 ml) and water (20 ml) were added, and a yellow liquid (2.86 g, 73%) was isolated by standard procedures. The product was purified by glpc on a column of 15% Carbowax on Chromosorb W operated at 75°. **3** was obtained as a colorless solid: mp 26.5–27°; δ^{CCl_4} 3.13 (s, 3) OCH_3, 1.05 (s, 6) CH_3, 0.90 (s, 9) *tert*-C_4H_9.

Anal. Calcd for $C_8H_{18}O$: C, 73.78; H, 13.93. Found:[13] C, 73.95; H, 13.95.

Rate Measurements.—Reaction solutions were 0.02 to 0.04 M in alkyl halide, arranged so that the base was always in at least tenfold excess. Solutions were prepared as previously described,[2] except that for $NaSC_2H_5$ runs neat ethanethiol was used, being measured by pipet. In $NaSC_2H_5$ runs, free ethanethiol was always present, from 1.5 to 2.0 equiv of C_2H_5SH being used per equivalent of $NaOCH_3$. In solvolysis runs, excess 2,6-lutidine was always present to neutralize the hydrogen chloride formed. Aliquots (5.0 ml) of the reaction solution were sealed in glass ampoules which had been flushed with nitrogen before sealing.

For $NaOCH_3$ and solvolysis runs, the contents of the chilled ampoules were poured into 30 ml of hexane, to which 5 ml of 15% nitric acid and 40 ml of water were then added. After stirring, potentiometric titration with standard $AgNO_3$ solution was carried out directly. For $NaSC_2H_5$ runs, the contents of the chilled ampoules were poured into 10 ml of hexane in a separatory funnel, 20 ml of water was added, the aqueous phase was separated and washed with 10 ml of diethyl ether, 1 ml each of concentrated nitric acid and of 30% hydrogen peroxide were added, the solutions were allowed to stand overnight, and they were

(5) L. F. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc. B*, 1084 (1967).

(6) J. F. Bunnett, *Surv. Prog. Chem.*, **5**, 61 (1969).

(7) D. L. Eck, unpublished work at Washington State University.

(8) C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K.-U. Yang, *J. Org. Chem.*, **36**, 887 (1971).

(9) G. Calingaert, H. Soroos, V. Hnizda, and H. Shapiro, *J. Amer. Chem. Soc.*, **66**, 1389 (1944).

(10) H. C. Brown and A. Stern, *ibid.*, **72**, 5068 (1950).

(11) Butlerow, *Justus Liebigs Ann. Chem.*, **177**, 184 (1875); Beilstein, **I**, 159.

(12) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, Netherlands, 1950, p 133.

(13) Analysis was by Micro-Tech Laboratories, Skokie, Ill.

then titrated with standard $AgNO_3$ solution. Plots of ln $(V_\infty - V_t)$ vs. time were linear and the negatives of their slopes, obtained by linear regression analysis, were taken as pseudo-first-order rate coefficients (k_ψ).

Product Analysis.—Reaction solutions prepared as for kinetics were sealed in ampoules which were kept in the thermostat for at least 10 half-lives. The ampoules were cooled and the contents poured into 15 ml of chlorobenzene. The organic phase was extracted with water (one 25-ml and two 10-ml portions), the organic phase was dried over anhydrous Na_2SO_4 (for $NaOCH_3$ and solvolysis runs) or over KOH (for $NaSC_2H_5$ runs), and portions were analyzed by glpc. An Aerograph Model 204 apparatus was used, with a 91-cm column of 5% SE-30 silicone rubber and 5% Bentone 34 clay on Chromosorb P, operated at a temperature of 55°. Molar responses were determined vs. benzene as internal standard. Samples taken at various time intervals showed no variation of product composition with time; the products are thus stable under the reaction conditions. The reaction temperature for both kinetic and product studies was 69.9° unless otherwise stated.

Because **1b** and **1c** are more reactive than **1a**, it was probable that appreciable reaction occurred at room temperature during preparation and sealing in ampoules of reaction solutions. In a few experiments, the technique was altered so as to effect mixing at 69.9°, but the product proportions observed were substantially the same as by the usual technique.

Results

In addition to results presented in Part A, we set forth in Table II kinetic data concerning the reaction

TABLE II
REACTION OF 2-IODO-2,3,3-TRIMETHYLBUTANE
(1c) WITH $NaOCH_3$ IN METHANOL AT 25.0°

[NaOCH₃], M	$10^4 k_\psi$, sec⁻¹
Nil[a]	8.54
0.108	8.40
0.216	8.20
0.432	7.29
0.810	6.89

[a] 2,6-Lutidine present.

of iodide **1c** with $NaOCH_3$ in CH_3OH at 25.0°. It is to be noted that the rate coefficient *drops* continuously; the drop is somewhat steeper at higher $NaOCH_3$ concentrations.

Discussion

We first examine two models to which we tried to fit our data, and then discuss the relevance of the data to some other problems.

The Simple Model of E1–SN1 Solvolysis Plus E2.—The essential feature of this model is that it provides for independent E1–SN1 and E2 components of reaction, according to eq 1, in which k_S^* pertains to

$$k_\psi = k_S^* + k_E[B] \qquad (1)$$

solvolysis and k_E to the E2 component. The effect of salts on k_S^* is not specified, except that the effects of two or more salts be additive. Whether or not anionic bases affect the proportions of olefin and ether formed from the carbonium ion intermediate is also not specified. A model of this type gave an excellent account of the $NaSC_2H_5$ data in an analogous study involving benzyldimethylcarbinyl chloride and a fair account of the $NaOCH_3$ data.[2]

This model calls for the kinetic effects of $NaClO_4$ and $NaOCH_3$, or of $NaClO_4$ and $NaSC_2H_5$, admixed, to be additive. Experimentally, however, they are

less than additive. This is shown in Table III. Clearly models of this type are not serviceable.

TABLE III

	$10^4 k_\psi$, sec⁻¹	$10^4 k_\psi$, sec⁻¹
0.552 M NaClO₄	13.6	13.6
0.802 M NaOCH₃	4.9	
0.368 M NaSC₂H₅		8.6
Sums	18.5	22.2
Actual for mixtures (Table I)	10.4	16.4

A Model of E1–SN1 Plus E2, with Anionic Bases Allowed to Have Negative Salt Effects.—Figure 1 and studies by Bunton and coworkers[8,14] indicate that $NaOCH_3$ may have a negative salt effect on solvolysis rates in methanol. This suggests the possibility that a negative salt effect by $NaOCH_3$ might be superimposed on a positive salt effect by $NaClO_4$ according to eq 2,

$$k_\psi = k_S(1 + b[NaClO_4])(1 - m[NaOCH_3]) + $$
$$k_E[NaOCH_3] \qquad (2)$$

in which k_S is the rate coefficient for solvolysis in the absence of salts, k_E is the E2 coefficient, and b and m are salt effect parameters.[15] Apart from the fact that a model of this sort cannot account for the rate maximum for $NaOCH_3$ in Figure 1 or the curvature for $NaSC_2H_5$, it leads to inconsistent estimates of k_E from reactions at various $NaClO_4$ concentrations.

Relevance to the Scheme of Sneen and Robbins.—Our results are reason for caution in accepting the mechanistic conclusions of Sneen and Robbins,[16] who aver that E2 and SN2 reactions of α-phenylethyl bromide proceed via a common intermediate, an ion pair. A principal element of support for their interpretation was their finding that the apparent second-order rate coefficient for reaction with $NaOC_2H_5$ in ethanol diminishes in relative magnitude from 1.0 at 0.1 M $NaOC_2H_5$ to 0.4 at 1.1 M $NaOC_2H_5$. They assumed that "normal salt effects" are minimal at the levels of $NaOC_2H_5$ concentration used in their investigation. The present work suggests that *abnormal* salt effects may also need to be taken into account.

If one sought to fit the present cases to the interpretation of Sneen and Robbins, he might take the downward slope of the $NaSC_2H_5$ plot in Figure 1 as evidence of approach to a rate plateau at which rate would be limited by the rate of ionization of **1a**. The curved plot for $NaOCH_3$ might be given a similar interpretation, the approach to a rate plateau being thought to be superimposed on a slight overall negative salt effect. However, rate plateaus at different heights would need to be assigned to the two plots, but that is inconsistent if both plateaus pertain to the same ionization process.

$NaSC_2H_5$ vs. $NaOCH_3$ as Elimination-Inducing Reagents.—As discussed in Part A, the drop in the fraction of olefin **2** in the product mixture caused by addition of $NaClO_4$ to reaction mixtures 0.802 M in $NaOCH_3$ or 0.368 M in $NaSC_2H_5$ (Table I) suggests a substantial E2 component. It remains to consider

(14) P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

(15) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956).

(16) R. A. Sneen and H. M. Robbins, *ibid.*, **91**, 3100 (1969).

why the plot in Figure 1 for the mercaptide base is so much steeper than for the alkoxide base. Is it because the E2 rate coefficient for the sulfur base is very much greater? Or is it because $NaSC_2H_5$ has a very favorable salt effect on ionization, whereas $NaOCH_3$ has a rather unfavorable one? We do not feel that a firm decision can be made because of the unsatisfactoriness of the various models. On the whole, however, it appears that the data are better explained in terms of a distinctly higher E2 rate coefficient for the sulfur base. Thus, the rate of change of olefin fraction in Table I is greater for $NaSC_2H_5$ than for $NaOCH_3$, and the former is less than half the concentration of the latter.

If this judgment is correct, it is noteworthy that the higher E2 reactivity of $C_2H_5S^-$ than of CH_3O^- persists even when the substrate is highly hindered about C_α; the carbon to which chlorine is attached in **1a** is both tertiary and neopentylic. Such an out-

come is not compatible with the "E2C" mechanism which has been proposed by other workers for certain eliminations induced by reagents of relatively low basicity.[17] We have earlier reported that **1b** undergoes E2 elimination with chloride ion in acetone or dioxane faster than with its less hindered analog, *tert*-butyl bromide,[18] and we have made similar observations with respect to secondary alkyl halides and tosylates.[19] These studies provide no support for the E2C mechanism. Reasons for the surprisingly high E2 reactivity of mercaptide ions in certain eliminations have been discussed elsewhere.[6]

Registry No.—**1a**, 918-07-0; **1b**, 16468-75-0; **1c**, 27705-19-7; **2**, 594-56-9; **3**, 27705-21-1.

(17) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968); G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(18) D. Eck and J. F. Bunnett, *ibid.*, **91**, 3099 (1969).

(19) J. F. Bunnett and D. L. Eck, unpublished observations.

Reactions of Bicyclo[2.1.0]pentane and Bicyclo[4.1.0]heptane with Hydrogen Chloride. Cleavage of Cyclopropane Rings[1a]

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The products of the reaction of bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II) with HCl in the vapor phase and with concentrated hydrochloric acid in a two-phase system have been studied. In the case of I, both cyclopentene and cyclopentyl chloride were obtained. In the case of II, nonthermodynamic mixtures of six-membered and seven-membered olefins and chlorides were obtained. It is proposed that the olefins arise primarily *via* quasiheterolytic six-membered cyclic transition states and that the chlorides arise *via* pathways of somewhat greater heterolytic character. Relief of strain in the ground state and nonbonded interactions and strain in the transition state are invoked to explain the relative amounts of internal and external cleavage of the three-membered ring as well as product distributions.

In connection with our work on the chlorination of bicyclo[*n*.1.0]alkanes,[1c,2] we have also investigated the reaction of hydrogen chloride with bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II). We wish to report our results since they are divergent from previously reported ones in at least one important respect, and since they serve to further elucidate the behavior of cyclopropanes in ring-opening reactions.

Cleavages of cyclopropyl compounds by acids or other electrophiles have been extensively studied.[3-9] Where rationales have been advanced,[4,6a] the course of the re-

action has been discussed in terms of polarization of the three-membered ring by the incoming electrophile. More recently[9] anti-Markovnikov ring opening of the cyclopropane in a tricyclo[3.2.2.0^{2,4}]nonyl system has been interpreted in terms of steric inhibition to normal collapse of a protonated cyclopropyl intermediate.

We have studied the reactions of I and II with HCl under conditions which are not conducive to normal ionic modes of reaction. Nevertheless, the results parallel those obtained under more ionic conditions[4] in many ways.

Results

Reaction between HCl and bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II) was brought about in several ways. In one approach, HCl vapor was added slowly to an excess of refluxing hydrocarbon and the two vapors were mixed, under anhydrous conditions, in a glass reaction chamber heated by sun lamps. These reactions were performed in a modification[1c] of a vapor phase chlorination apparatus designed by Roberts and Mazur.[10] In another approach, equimolar amounts of 12 M hydrochloric acid and I at 10° or II at 25° were shaken vigorously for 6 hr. In addition II was reacted with a twofold excess of anhydrous HCl in a glass ampoule, filled on a vacuum line, sealed, and heated

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