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Kinetics, Products, and Mechanisms of Reaction of *tert*-Butyl Chloride with Sodium Methoxide in Methanol and Dimethyl Sulfoxide/Methanol Solvents[1,2]

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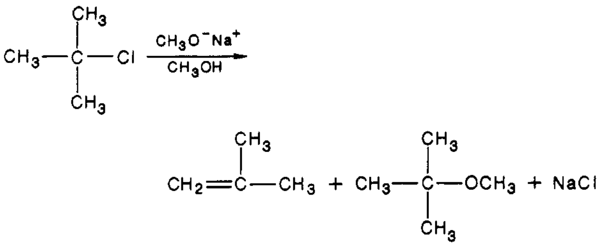
The rate of reaction of *tert*-butyl chloride with methanolic sodium methoxide shows little variation with base concentration up to 1 mol/L, but the presence of MeONa causes the product composition to shift strongly toward 2-methylpropene. What mechanisms prevail is uncertain; one possibility is that as [MeONa] increases the E2 mechanism participates to a small but increasing extent while E1–S_N1 solvolysis continues at a nearly constant rate. When the solvent is enriched in dimethyl sulfoxide, the overall rate increases robustly with [MeONa] in nonlinear fashion, with increasing slope, and the product is almost entirely the alkene.

Wanting better to understand the comparative reactivities of methoxide and ethanethiolate ions as reagents to effect β-elimination, we undertook a thorough study of the kinetics and products of reactions of sodium methoxide with *tert*-butyl chloride (*t*-BuCl) in three solvent systems. We did a parallel study with sodium ethanethiolate base, as reported in the following paper in this issue.

Methanol. This system (eq 1) is of a sort regularly discussed in elementary textbooks of organic chemistry. Because this is a prototype system, and because of its relevance to further work that we planned, we chose to study it thoroughly. We have found kinetics much as the textbooks would lead one to expect, but variation of product composition as base concentration is changed that may complicate its discussion early in an elementary course.



$$(CH_3)_3C{-}Cl \xrightarrow[CH_3OH]{CH_3O^-Na^+} CH_2{=}C(CH_3){-}CH_3 + CH_3{-}C(CH_3)_2{-}OCH_3 + NaCl \quad (1)$$

The Literature. There are few kinetic data in the literature to support textbook discussions of the dependence of the combined rates of substitution and elimination on lyate ion concentration. Even fewer determinations of product proportions have been reported.

In earlier years, especially during the 1930s, many determinations of rates of solvolysis of tertiary alkyl halides were made, in pure solvents and in solvent mixtures. A few determinations of kinetic response to added lyate ions were made. Many of the earlier determinations were reviewed by Streitwieser[3] and by Ingold.[4] Some of the more recent determinations are cited.[5,6] One of the significant earlier papers having to do with lyate ion effects is that of Benfey, Hughes, and Ingold.[7] Seldom were product proportions determined before the advent of gas–liquid chromatography in the mid-1950s.

Table I. Reactions of *tert*-Butyl Chloride with Sodium Methoxide in Methanol: Kinetic and Product Data[a]

[NaOMe], M	$k_\psi/10^{-4}$, s^{-1}	alkene, %	ether, %	Δ,[b] %	$k_\psi^E/10^{-4}$, s^{-1}
nil[c]	2.15 ± 0.19	26.2	73.8	0.7	0.56
0.20	2.40 ± 0.19				
0.25	2.30 ± 0.01	37.1	62.9	8.1	0.85
0.30	2.26 ± 0.15				
0.39	2.36 ± 0.16				
0.49	2.61 ± 0.25				
0.50	2.56 ± 0.13	41.4	58.6	0.6	1.06
0.68	2.39 ± 0.07				
0.75	2.58 ± 0.03	48.3	51.7	6.6	1.25
0.90	2.64 ± 0.07	47.8	52.2	3.2	1.26
1.00	2.74 ± 0.11				

[a] All reactions at 70 °C, with [*t*-BuCl] ca. 0.02 M. [b] Discrepancy between moles of Cl^- (by titration) and sum of moles of alkene and moles of ether (by GLC) in "infinity" samples. [c] Two runs, one with 0.022 M 2,6-lutidine, the other with 0.034 M 2,6-lutidine, gave nearly identical rate constants; the rate constant listed is the mean value.

Of special interest to us is a report[8] of the kinetics and products of reaction of some trimethylnorbornyl chlorides with methanolic sodium methoxide at diverse concentrations. We also recall a study of the rates and products of reaction of sodium methoxide, at several concentrations, with benzyldimethylcarbinyl chloride.[9]

Results. Our kinetic and product determinations are summarized in Table I. Reaction rates were determined under pseudo-first-order conditions, that is, with *t*-BuCl in severe deficiency with respect to MeONa, and the progress of reactions was followed by titration of chloride ion. Products were determined by gas chromatography. For reactions in the absence of MeONa, 2,6-lutidine was supplied in excess over the *t*-BuCl to neutralize the HCl product and thwart acid-catalyzed equilibration among the products.[10]

Comment. Two features of our data are noteworthy. Overall reaction rate increases very little as [MeONa] rises

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[1] Based in part on the Dissertation of C. A. Migdal, University of California, Santa Cruz, CA, June 1985.

[2] Financial support from the National Science Foundation (Grant CHE-8311582) is gratefully acknowledged.

[3] Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571.

[4] Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; Chapter VII.

[5] Biordi, J.; Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1962**, 4291.

[6] Turnquest, C. R.; Taylor, J. W.; Grimsrud, E. P.; Williams, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 4133.

[7] Benfey, O. T.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1952**, 2494.

[8] Beltramé, P.; Bunton, C. A.; Dunlop, A.; Whittaker, D. *J. Chem. Soc.* **1964**, 658.

[9] Bunnett, J. F.; Davis, G. T.; Tanida, H. *J. Am. Chem. Soc.* **1962**, *84*, 1606.

[10] It has been shown, in regard to solvolysis of benzyldimethylcarbinyl chloride in methanol,[9] that amines ammonia, piperidine, *n*-butylamine, and 2,6-lutidine have equal (and presumably negligible) effects on product proportions.

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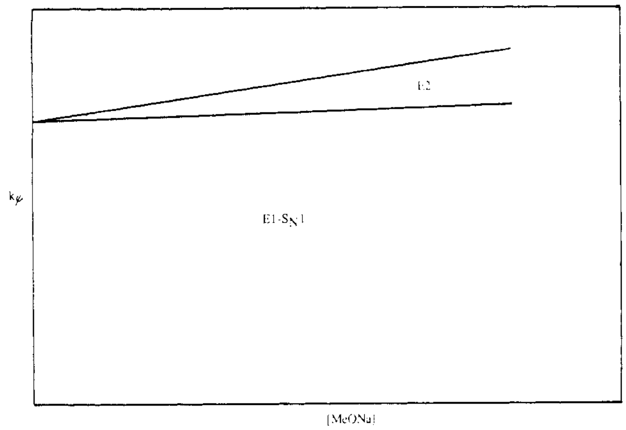

Figure 1. Schematic representation of kinetic contributions of the E1-S_N1 (solvolysis) mechanism and the E2 mechanism, according to the mixed-mechanisms model.

Scheme I

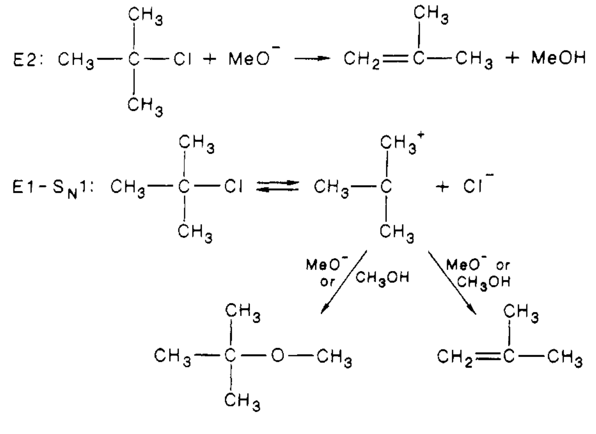

Table II. Reactions of *tert*-Butyl Chloride with Sodium Methoxide in 36.8 mol % Dimethyl Sulfoxide/Methanol: Kinetic and Product Data[a]

[NaOMe], M	$k_\psi/10^{-4}$, s^{-1}	alkene, %	ether, %	Δ,[b] %	$k_\psi^E/10^{-4}$, s^{-1}
nil[c]	0.81 ± 0.14	50.0	50.0	0.2	0.40
0.20	1.52 ± 0.05				
0.30	1.90 ± 0.06	89.5	10.5	2.5	1.70
0.40	2.65 ± 0.07				
0.55	2.66 ± 0.09	96.6	3.4	6.1	2.57
0.60	2.94 ± 0.07	95.2	4.8	3.1	2.80
0.65	3.45 ± 0.14	98.9	1.1	0.7	3.41
0.70	4.11 ± 0.21	98.9	1.1	0.5	4.06
0.80	4.59 ± 0.10				
0.90	6.16 ± 0.38	95.9	4.1	1.6	5.91
1.00	6.89 ± 0.30	96.2	3.8	9.6	6.63

[a] All reactions at 70 °C, with [*t*-BuCl] ca. 0.02 M. [b] Discrepancy between moles of Cl^- (by titration) and sum of moles of alkene and moles of ether (by GLC). [c] Mean of two runs, in the presence of 0.020 or 0.022 M 2,6-lutidine.

from 0 to 1.00 M, but product composition changes considerably, from about three-quarters ether/one-quarter alkene in the absence of MeONa to roughly half-and-half at 0.90 M MeONa.

Treating the kinetic data by the equation of Fainberg and Winstein[11] (eq 2), the spirit of which would be to attribute the modest increase in overall rate to a salt effect, one evaluates slope parameter b as 0.23 ± 0.05 M^{-1}. The slight increase in rate is thus statistically significant.

$$k_t = k_t^\circ\{1 + b[\text{salt}]\} \qquad (2)$$

We suggest two extreme models of interpretation, recognizing that actual behavior may not conform exactly to either of them.

The E1-S_N1 model holds that the reaction is essentially of E1-S_N1 character throughout the range of sodium methoxide concentrations studied and attributes the change in product composition to a change in the relative rates of progression of the *t*-butyl cation to 2-methylpropene and to *tert*-butyl methyl ether as methoxide concentration changes. This model is sketched in Scheme I, lower part.[12]

On this hypothesis, methoxide ion excels methanol in formation of both products, but especially of the alkene. We attempted to calculate, by the method of ad eosdem competition,[13] the relative reactivity of MeONa versus MeOH in effecting conversion of the *tert*-butyl cation to the alkene and to the ether. The appropriate plot of product data[13] (not shown) is scattered, and there is large uncertainty in the slope parameter; nevertheless, it indicates that methoxide surpasses methanol in forming the alkene from the cation about 90-fold, and in forming the ether from the cation about 20-fold.

The mixed-mechanisms model postulates that the slight dependence of overall rate on [MeONa] represents an overlay of some E2 reaction on an underlying solvolysis (E1-S_N1) reaction whose rate is little affected by MeONa. See Scheme I. The E2 process, which forms only the alkene, gradually grows in significance as base concentration increases. This idea is sketched in Figure 1. That the lyate salt should accelerate solvolysis very little would be remarkable only inasmuch as lyate ions have been observed to have *negative* salt effects on solvolyses. Thus, NaOH in aqueous dioxane represses the solvolysis of several *p*-toluenesulfonate esters.[14] A precedent closer to the present work is the report of Beltramē et al.[8] that methanolic NaOMe retards the solvolysis of isobornyl chloride, 0.8 M MeONa reducing the rate to about half of its value in neutral methanol.

To this model we can attach a further postulate, namely, that the product proportions from the E1-S_N1 component are independent of base concentration. If so, one can allocate the alkene formed between the E1-S_N1 and E2 routes with reference to the amount of ether formed. For the [MeONa] at which products were determined (Table I), the percentages of alkene formed by E2 are thereby calculated to be, respectively, 0, 14.8, 21.6, 29.9, and 29.3%. These percentages are roughly linear with [MeONa] (plot not shown), as one would anticipate from Figure 1, but the data are scattered. From this possible E2 fraction of the alkene formed at 0.9 M MeONa, and data in Table I for that base concentration, one would reckon the second-order rate constant for the E2 reaction with sodium methoxide to be 4.1 × 10^{-5} M^{-1} s^{-1}.

Our Judgment. The data of Table I by themselves do not tell which if either of these models is the best representation of the reaction system.[17] The mixed-mecha-

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[11] Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763.

[12] The *tert*-butyl cation in Scheme I should be understood to be the free ion, or a solvent-separated or contact ion pair, or some combination thereof. Our data do not give insight into how the carbocation may be associated in the systems studied.

[13] Bunnett, J. F. *Investigation of Rates and Mechanisms of Reactions*, 4th ed.; Bernasconi, C. F., Ed.; John Wiley & Sons; New York, 1986; p 206.

[14] Duynstee, E. F.; Grunwald, E.; Kaplan, M. L. *J. Am. Chem. Soc.* **1960**, *82*, 5654.

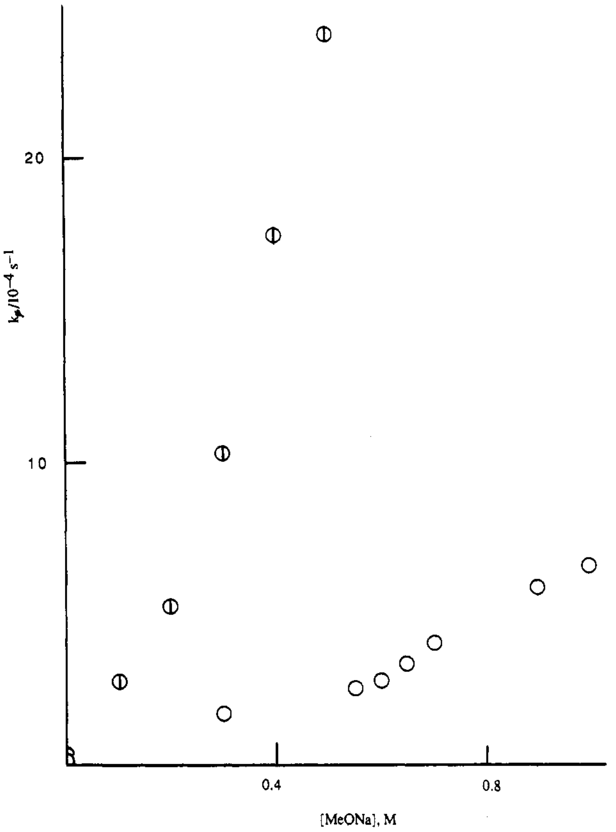

Figure 2. Pseudo-first-order rate constants for reactions of *t*-BuCl with MeONa in 36.8 mol % Me_2SO/MeOH (open circles) and in 64.2 mol % Me_2SO/MeOH (barred circles).

nisms model is, however, in better accord with other data, especially the negative salt effect by MeONa in MeOH observed by Beltramé et al.[8] and the clear evidence of E2 behavior in solvents containing a considerable fraction of dimethyl sulfoxide, which we report below.

It may well be that the mixed-mechanisms model obtains, but with the products from the E1–S_N1 component becoming enriched in alkene as [MeONa] increases.

For the purpose of considering reactivity in olefin-forming elimination, regardless of mechanism, the parameter $k_\psi{}^E$ is useful. It is the pseudo-first-order rate constant multiplied by the fraction of elimination and is listed for each sodium methoxide concentration in Table I for which we have both kinetic and product data.

Results. 36.8 mol % Dimethyl Sulfoxide/Methanol. Our kinetic and product data are summarized in Table II. A feature of passing interest is that the rate of solvolysis in this solvent in the absence of base is less than half the rate in methanol. It is known[18] that admixture of dimethyl sulfoxide with an hydroxylic solvent diminishes solvolysis rates.

The overall rate increases strongly with increase of sodium methoxide concentration, as shown in Figure 2 (open circles). The plot has a "dog leg" appearance, with a steep increase in slope at about 0.6 M NaOMe; alternatively, the data might be described as curvilinear, concave upward, with substantial scatter of points. A plot (not shown) of log k_ψ versus log [MeONa] also has a dog-leg appearance; the slope is about 0.6 below 0.6 M MeONa, and 1.6 above that concentration.

As for products, equal amounts of 2-methylpropene and *tert*-butyl methyl ether are formed in the absence of MeONa, but in the presence of that base, 90% or more of the alkene is formed, with the ether being generated only to the extent of 1–4% of higher base concentrations.

Comment. The parameter representing overall olefin-forming elimination reactivity, regardless of mechanism, evaluated as k_ψ times fraction of alkene product, and symbolized $k_\psi{}^E$, is listed in Table II. It increases strongly as [MeONa] increases.

As to models of reaction mechanism, one should consider for this solvent system the same two postulated above for reactions in methanol. The E1–S_N1 model, if applicable in this solvent rich in dimethyl sulfoxide, would necessitate that MeONa exert a substantial *positive* salt effect on solvolysis. The mixed-mechanisms model would attribute the strong proclivity to form alkene when MeONa is present to a combination of a substantial rate constant for E2 reaction and a strong [MeONa] effect on the proportionation of the *tert*-butyl cation between alkene and ether products.

Again we lack compelling evidence as to which model is more closely approximated by the actual events, but we will discuss the data in mixed-mechanism terms, with principal attention to the E2 component, which would predominate at higher [MeONa]. The upward curvature in Figure 2 appears to represent an activity coefficient effect, which might be discussed in acidity function terminology.[19] It probably is related to the modest supply of methanol molecules in this solvent system, fewer than two per dimethyl sulfoxide molecule. The sulfoxide is doubtless considerably solvated by methanol. The methoxide ion normally acquires considerable methanol of solvation: three MeOH per MeO^- in methanol itself.[20] and about two MeOH per MeO^- in MeOH/Me_2SO mixtures.[21] Accordingly the methoxide ion at higher [MeONa] is probably short of its optimum solvation and is at an elevated level of Gibbs free energy with an elevated activity coefficient.[22]

In such circumstances, one might choose to plot the logarithm of the observed rate constant against the appropriate acidity function. It happens, however, that the acidity functions that have been established for MeOH/Me_2SO mixtures pertain to solutions containing a low and usually constant concentration of methoxide ion and varying solvent composition.[19] We do, however, note a study by Cram and co-workers[23] in which rates of proti-

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(15) A reviewer has suggested that uncertainties that we have expressed regarding the salt effect of MeONa in this paper and that of EtSNa in the following paper in this issue could have been resolved by conducting kinetic runs at constant ionic strength. By intent, we did not do so, because we were aware that salt effects for solvolyses in methanol are highly specific to the salt employed. For example, $NaClO_4$ has a much larger kinetic (accelerating) effect on the decomposition of benzyldimethylcarbinyl chloride in methanol than does NaOMe.[9] Also, Bunton et al.,[16] who studied salt effects on the methanolysis of several alkyl halides prone to solvolyze, observed Winstein *b* parameters that differed substantially between different salts; thus, for methanolysis of 2-methyl-*exo*-2-norbornyl chloride, the *b* parameters were 1.3 for lithium nitrate but 6.3 for lithium perchlorate. Certainly an exploration of salt effects on the reactions of MeONa and EtSNa with *t*-BuCl in methanol would be interesting, but whether the data obtained would contribute additional clarity to mechanistic interpretations is uncertain.

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

(17) Joseph R. Gandler (California State University, Fresno, CA) has suggested in conversation that kinetic and product studies of the behavior of fully deuterated *t*-BuCl should provide evidence for a decisive choice of model; the E2 reaction should be retarded much more by the kinetic isotope effect than the E1–S_N1.

(18) Blandamer, M. J. *Adv. Phys. Org. Chem.* **1977**, *14*, 331.

(19) Bowden, K. *Chem. Rev.* **1966**, *66*, 119.

(20) Gold, V.; Grist, S. *J. Chem. Soc. B* **1971**, 1666.

(21) Baltzer, L.; Bergman, N.-A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 313.

(22) This is a well-recognized effect. See, for example: Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979; p 159.

Table III. Reactions of *tert*-Butyl Chloride with Sodium and Potassium Methoxides in 64.2 mol % Dimethyl Sulfoxide/Methanol: Kinetic and Product Data[a]

[MeONa], M	[MeOK], M	$k_\psi/10^{-4}$, s^{-1}	alkene, %	ether, %	$k_\psi^E/10^{-4}$, s^{-1}
nil	nil	0.237 ± 0.037[b]	76[b,c]	24[b,c]	0.18
	0.05[d]	1.93 ± 0.04	99	1	1.91
0.10		2.82 ± 0.05	99	1	2.79
	0.10	3.05 ± 0.04	100	0	3.05
0.20		5.3 ± 0.3	99	1	5.3
	0.20	7.2 ± 1	100	0	7.2
0.30		10.3 ± 0.4	100	0	10.3
	0.30	11.4 ± 0.2	100	0	11.4
0.40		17.5 ± 0.6	100	0	17.5
	0.40	17.7 ± 0.3	100	0	17.7
0.50		24.1 ± 0.6	100	0	24.1
	0.50	24.5 ± 0.8	100	0	24.5

[a] All reactions at 70 °C, with [*t*-BuCl] ca. 0.02 M. [b] Average of three runs, conducted with 2,6-lutidine (0.02–0.10 M) and 2,6-lutidinium bisulfate (0.05 M) present. [c] Average Δ (see footnote *b*, Table II) was 9%. [d] Dibenzo-18-crown-6 (0.05 M) was present.

um–deuterium exchange of (+)-2-methyl-3-phenylpropanenitrile and related substrates were determined in MeOH/Me_2SO mixtures with MeONa or MeOK concentration sometimes varied. The measurements closest to ours in character were for 97% Me_2SO/3% MeOH and, thus, not close enough to warrant a plot of our data versus theirs; it is, however, noteworthy that they observed a dog-leg plot of log *k* versus log [MeONa] or log [MeOK], thus resembling our data somewhat.

If one attributes the increased reactivity at higher [MeONa] (Figure 2) to E2 reaction, assuming the E1-S_N1 rate to be insensitive to base concentration, one interprets the slopes of the two quasi-linear segments of the plot as second-order rate constants for E2; they are 3.6×10^{-4} M^{-1} s^{-1} below 0.6 M MeONa and 9.8×10^{-4} M^{-1} s^{-1} above that concentration.

Results. 64.2 mol % Dimethyl Sulfoxide/Methanol. We determined product compositions and pseudo-first-order rates of reaction of *t*-BuCl in the solvent, buffered with 2,6-lutidine and 2,6-lutidinium bisulfate, and with several concentrations of MeONa and MeOK. Our principal data are presented in Table III.

As to products, 2-methylpropene is favored 3/1 over *tert*-butyl methyl ether in the buffered solvent. In the presence of the metal alkoxide bases, alkene formation occurred almost exclusively.

We pointed out above that the rate of solvolysis in the absence of MeONa is depressed on changing the solvent from methanol (Table I) to 36.8% Me_2SO/MeOH (Table II). We now see that it is further depressed in 64.2% Me_2SO/MeOH.

It is evident in Table III that rate constants in MeOK solutions are nearly equal to those in MeONa solutions at equal concentrations. This insensitivity to the identity of the cation is noteworthy in a solvent prone to promote ion pairing. A similar effect was observed by Cram and coworkers[23] for reactions in 97% Me_2SO/MeOH.

In Figure 2 (barred circles), the overall pseudo-first-order rate constant is plotted as a function of [MeONa]. The plot is curved in the same sense as the plot in Figure 2 for reactions in 36.8 mol % Me_2SO, but the rate constants are much greater in 64.2 mol % Me_2SO. Making assumptions as detailed above, one could interpret the slopes of the two segments of the 64.2 mol % plot as E2 rate constants: 2.5×10^{-3} M^{-1} s^{-1} up to 0.2 M MeONa and 6.5×10^{-3} M^{-1} s^{-1} between 0.3 and 0.5 M MeONa.

Comment. Although in 64.2 mol % dimethyl sulfoxide/methanol the product of reaction with MeONa is almost entirely alkene, we list in Table III the parameter k_ψ^E for the sake of parallelism with Tables I and II.

Our comments above about reaction mechanism in 36.8 mol % Me_2SO/MeOH pertain also to the present solvent system. The facts that the product is almost entirely the alkene and that rates with the alkoxide bases are much higher than in the solvent of lower Me_2SO content suggest that the mechanism in 64.2 mol % Me_2SO/MeOH is E2 with scarcely any E1-S_N1 component.

Overall Significance. No doubt the significance of our data, as of any other, is in the mind of the beholder. Besides aspects discussed above, they are very interesting to us for comparison with corresponding reactions with sodium ethanethiolate as base, as reported in the accompanying paper.[24]

Experimental Section

Materials. *tert*-Butyl methyl ether, bp 55 °C, was made by acid-catalyzed reaction of methanol with *tert*-butyl alcohol, after Norris and Rigby.[25] 2,6-Lutidinium bisulfate, mp 160–161 °C, was made by combining 2,6-lutidine (11.3 mL) and aqueous sulfuric acid (12 M; 5.0 mL) in 50 mL of chilled absolute ethanol; the crystals that separated were collected, recrystallized from ethanol (30 mL), collected, washed with cold acetone, and dried in a vacuum desiccator; neutral equivalent: calcd 205.2; found 205.8. *tert*-Butyl chloride (Aldrich Chemical Co.) was fractionally distilled, a middle cut being taken at 50 °C; its purity was confirmed by gas chromatography (GC). 2,6-Lutidine (Aldrich Chemical Co.) was stirred overnight with crushed potassium hydroxide and then distilled, a middle cut of bp 143 °C being taken; its purity was confirmed by GC and its authenticity by NMR. Cyclohexene (often used as a GC internal standard) was a Mallinckrodt product fractionally distilled, a middle cut of bp 82 °C being collected; its purity was verified by GC and NMR. 2-Methylpropene, to serve as an authentic sample for calibration of analyses, was obtained as a compressed gas from J. T. Baker Chemical Co. and was used as received. Dibenzo-18-crown-6 ether (Aldrich Chemical Co.) was recrystallized from toluene with use of activated charcoal to remove a brownish impurity; mp 161–161.5 °C (lit.[26] mp 163–164 °C). Methanol, reagent grade, was dehydrated by the magnesium turnings method.[27] Dimethyl sulfoxide, generously donated by Crown Zellerbach Corp., was stirred for 48 h with CaH_2 and then distilled from CaH_2 under vacuum, argon gas being admitted when receivers were changed; a middle cut of bp 30 °C (0.15 Torr) was taken; it was stored in the dark under argon. Methanolic sodium methoxide solution was made by reaction of sodium metal (pared, rinsed with pentane and then with methanol) with purified methanol and filtered through a fritted glass filter; its concentration was determined by titration with standard HCl solution. Methanolic potassium hydroxide was similarly prepared, with the methanol being chilled to −15 to −5 °C during the reaction of K with MeOH. Solutions in dimethyl sulfoxide/methanol were prepared with the weight of each constituent being measured by weighing the volumetric flask before and after each addition, except that MeONa and MeOK were measured by the volumes of standard solutions in MeOH that were added.

Instruments and Methods. A Hewlett-Packard 5840A gas chromatograph was used throughout. Analyses were conducted with a Carbowax or Superox 0.1 coated capillary column, at 30 or 60 °C (column temperature), respectively; the injection port was at 150 °C and the flame ionization detector at 200 °C. Potentiometric titrations for chloride ion were performed, in solutions acidified with nitric acid, with a glass electrode and a silver wire

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(23) Cram, D. J.; Rickborn, B.; Kingsbury, C. A.; Haberfield, P. *J. Am. Chem. Soc.* **1961**, *83*, 3678.

(24) Bunnett, J. F.; Migdal, C. A. *J. Org. Chem.*, following paper in this issue.

(25) Norris, J. F.; Rigby, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 2088.

(26) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7071.

(27) Fieser, L. F. *Experiments in Organic Chemistry*, 3rd ed.; D. C. Heath & Co.: New York, 1957; p 289.

electrode, the titrant being a standard aqueous solution of silver nitrate. Proton NMR spectra were recorded on a JEOL EM360L spectrometer. Melting points and boiling points are uncorrected.

Kinetics Procedure. Besides the reactants mentioned in Tables I–III, most reaction solutions also contained a hydrocarbon to act as internal standard for product determination purposes; the internal standard was mostly cyclohexene, but sometimes methylcyclohexane.

For each run, the appropriate reaction solution was prepared at or about room temperature; 5-mL aliquots were dispensed into ampules of ca. 10 mL capacity, which were then cooled by means of dry ice, flushed with N_2, and sealed with a torch.[28] The ampules for a run, usually 15 in number, were placed all at once in a thermostat at 70.0 ± 0.1 °C. At recorded times, ampules were removed, plunged into ice/water, and after 1 min placed (unopened) in storage in contact with dry ice or in a freezing cabinet at −20 °C. Usually 11 ampules were so removed during about 2.5 half-lives. The other four ampules were allowed to react for 10 half-lives. For analysis of its contents, an ampule was allowed to warm to perhaps 0 °C and carefully broken open, and its contents were transferred quantitatively to a separatory funnel containing 10 mL of CH_2Cl_2 and 5 mL of 12% aqueous HNO_3, rinsing of the ampule and its cap being performed with the nitric acid solution. The contents of the funnel were shaken, the dichloromethane layer was drawn off, and the aqueous layer was extracted with a second 10-mL portion of dichloromethane. The aqueous layer was transferred quantitatively to a 150-mL beaker, 2% aqueous nitric acid was added until the volume was about 50 mL, and then 50 mL of acetone was added. (The purpose of the acetone is to decrease the solubility of AgCl and thereby give a sharper titration end point.) The chloride ion in the solution was determined by potentiometric titration with silver nitrate.[29] The ampules so analyzed included two of the four that had been allowed to react for 10 half-lives, as "infinity" samples.

Plots of ln $(V_\infty - V_t)$, where V is the volume of $AgNO_3$ solution, versus time were uniformly linear; the negatives of their slopes were taken as pseudo-first-order rate constants.

Product Determination. For the most part, 2-methylpropene and *tert*-butyl methyl ether were identified by the identity of their GC retention times on two or more columns with those of authentic samples. In one case, the "infinity" solution from a reaction with 0.7 M MeONa in 36.8 mol % Me_2SO/MeOH was examined by proton NMR; the observed peaks and chemical shifts matched those of an authentic sample of 2-methylpropene.

Products present in "infinity" ampules were determined quantitatively by GC. Inasmuch as 2-methylpropene has a low boiling point, the ampules were opened while chilled (at ca. −78 °C for runs in MeOH, at ca. −15 °C for runs in Me_2SO-containing solvents) and capped with a rubber septum, and the contained solution was injected into the gas chromatograph by means of a precooled syringe. The determination was calibrated by injection of mixtures containing the alkene and the ether in known concentrations, precautions being taken to prevent escape of the volatile alkene during injection or during pauses. Analyses were found to be reproducible, and analyses of mixtures of known composition verified that they were accurate. The "infinity" ampule product compositions are those reported in Tables I–III.

Registry No. *t*-BuCl, 507-20-0; MeONa, 124-41-4.

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(28) Reference 13, p 215.

(29) That no significant decomposition of Me_2SO, to form substances reactive with silver ion, occurred during reactions involving MeONa is shown by the small magnitude of the Δ values listed in Table II. Observations reported by Alexander et al.[30] are of similar import.

(30) Alexander, R.; Ko, E. C. F.; Parker, A. J.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049.

Kinetics, Products, and Mechanism of Reaction of *tert*-Butyl Chloride with Sodium Ethanethiolate in Methanol and Dimethyl Sulfoxide/Methanol Solvents. Insight into the Occasional Superiority of Thiolate over Alkoxide Ions in Effecting E2 Eliminations[1,2]

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In three solvents, with EtSNa in great excess over *t*-BuCl, the pseudo-first-order rate constant is linearly related to [EtSNa]. The slopes, which can be taken as second-order rate constants, increase by 50% from methanol to 36.8 mol % Me_2SO/MeOH, and by 3.2-fold from that solvent to 64.2 mol % Me_2SO/MeOH. The product is overwhelmingly 2-methylpropene; some *tert*-butyl methyl ether is formed, but no *tert*-butyl ethyl sulfide. Comparison with data for reactions of sodium methoxide (with *tert*-butyl chloride) in the same three solvents shows that the thiolate reagent is more effective at inducing elimination in the two solvents richer in methanol, but that sodium methoxide surpasses it in the solvent rich in dimethyl sulfoxide. These results are compatible with the theory of the variable E2 transition state; there is no need to invoke the "E2C" mechanism to interpret them.

It was a third of a century ago that de la Mare and Vernon[3] shocked the world by their observation that benzenethiolate ion is more effective than ethoxide ion in producing 2-methylpropene from *tert*-butyl chloride (*t*-BuCl) in ethanol solution. It seemed contrary to reason that a weaker base should be more effective than a stronger one in a reaction that involves hydron[4] abstraction.

The E2C Hypothesis. Meanwhile Winstein, Darwish, and Holness[5] found halide ions to function surprisingly well as reagents to convert 4-*tert*-butylcyclohexyl *p*-toluenesulfonates to 4-*tert*-butylcyclohexene in acetone solution. They believed the unexpected elimination-inducing reactivity of halide ions to stem from their considerable nucleophilicity in acetone and proposed a mechanism of merged substitution and elimination, with a transition state much like that for S_N2 reactions but with concurrent

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(2) Based in part on the Dissertation of C. A. Migdal, University of California, Santa Cruz, CA, June 1985.

(3) de la Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc.* **1956**, 41.

(4) "Hydrons" comprise protons, deuterons, and tritons.

(5) Winstein, S.; Darwish, D.; Holness, N. J. *J. Am. Chem. Soc.* **1956**, *78*, 2915.