# Comparison of Mercaptide and Alkoxide Ions as Reagents for Olefin-Forming $\beta$ Elimination[1]

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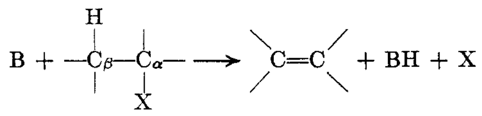
*Received July 21, 1966*

Rates of olefin-forming elimination, induced by methoxide and by thioethoxide ions, from benzyldimethylcarbinyl derivatives Ic and Id have been determined. The thioethoxide/methoxide reactivity ratio is found to depend on the leaving group in the reaction. For elimination to olefin II, the ratio is 6.5 with a good leaving group (Cl), 0.8 with a moderately good leaving group [$S(CH_3)_2^+$], and 0.05 with a poor leaving group ($SO_2CH_3$). These results are in accord with the hypotheses that these are normal E2 reactions and that the $RS^-/RO^-$ reactivity ratio is greater the lower the degree of bonding of base to hydrogen in the transition state. No support is found for the hypothesis that mercaptide ions are especially reactive in certain elimination reactions because of partial covalent interaction with $C_\alpha$ in the transition state.

In an E2 $\beta$ elimination, a nucleophile (or base) removes a proton from one carbon as a leaving group departs from an adjacent carbon atom. It was obviously to be expected that the reactivity of nucleophiles (bases) in bringing about elimination should parallel their affinity for protons, or basicity.[4]



$$B + -\overset{H}{\overset{|}{\underset{|}{C_\beta}}}-\overset{|}{\underset{X}{C_\alpha}}- \longrightarrow \;\rangle C=C\langle\; + BH + X$$

Consequently it was quite a surprise when de la Mare and Vernon[5] found that sodium thiophenoxide in ethanol effects elimination from *t*-butyl chloride about ten times faster than the stronger base, sodium ethoxide. Similar observations and more extensive kinetic detail have been reported by other investigators.[6-8] Also halide ions, not usually considered to be strong bases, have been found to be useful as dehydrohalogenation reagents in dipolar aprotic solvents.[9,10]

Rationalization of the high reactivity of rather weakly basic nucleophiles in $\beta$ eliminations was a challenge. Two alternative hypotheses were developed. One, taking note of the fact that the surprisingly effective reagents of rather low basicity are strong nucleophiles toward carbon, postulated covalent interaction of reagent with carbon in the transition state for elimination. The essence of the other was that nucleophilic reactivity toward hydrogen need not parallel the basicity of reagents.

According to the first hypothesis, elimination was initiated by attack of mercaptide or halide ion on $C_\alpha$, on the backside with respect to the leaving group. The reaction pathway was then considered to branch, one branch leading to substitution product in the usual S<sub></sub>N2 fashion and the other leading to olefin by association of nucleophile or leaving group with a $\beta$ hydrogen as all three separated from carbon. This hypothesis of merged substitution and elimination[11,12] has been restated in papers by Cromwell and co-workers[13,14] and other authors have subscribed to it.[15,16] Despite considerable experimental work on elimination in his laboratory,[17] Winstein appears to have made no claims for the "merged" mechanism since his original proposal.

According to the second hypothesis, eliminations induced by reagents of comparatively low basicity are normal E2 reactions, but for some reason certain reagents are more effective than might be expected from their basicity. The possibility that mercaptide ions are generally stronger than alkoxide ions as nucleophiles toward hydrogen, as they are toward carbon, was considered.[18] However, the fact that sodium thioethoxide in ethanol is much less effective than sodium ethoxide in catalyzing the isomerization of menthone to isomenthone[19,20] showed that such a relationship could not have general validity.[21]

It therefore seemed necessary to postulate that the $RS^-/RO^-$ reactivity ratio depended on the degree of bond formation between base and hydrogen in the transition state. In enolate ion formation from ketones, an endo-energetic step, the transition state probably lies close to the enolate ion on the reaction coordinate,[24] with a large degree of bonding of base to hydrogen, but, in E2 dehydrohalogenation of *t*-alkyl halides in alcoholic solvents, the transition state appears to involve relatively little bonding of base to hydrogen.[25] It seemed possible that mercaptide ions were relatively more effective the lower the degree of

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(1) (a) Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund. (b) Preliminary communication: J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc.*, 238 (1963).

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(3) Grateful recipient of a research scholarship from the Consiglio Nazionale delle Ricerche d'Italia, 1962–1963.

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 451.

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

(6) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1957); E. L. Eliel and R. G. Haber, *ibid.*, **81**, 1249 (1959).

(7) J. F. Bunnett, G. T. Davis, and H. Tanida, *ibid.*, **84**, 1606 (1962).

(8) *Cf.* E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 487.

(9) A. J. Parker, *Quart. Rev.* (London), **16**, 183 (1962).

(10) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Am. Chem. Soc.*, **86**, 1553 (1964).

(11) S. Winstein, D. Darwish, and N. J. Holness, *ibid.*, **78**, 2915 (1956).

(12) A. Hassner, N. H. Cromwell, and S. J. Davis, *ibid.*, **79**, 230 (1957).

(13) D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

(14) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963).

(15) E. L. Eliel and R. S. Ro, *Tetrahedron*, **2**, 353 (1958).

(16) R. U. Lemieux and D. R. Lineback, *Can. J. Chem.*, **43**, 94 (1965).

(17) S. Winstein, P. Beltrame, G. Biale, R. Cetina, D. Darwish, S. Smith, I. D. R. Stevens, and J. Takahashi, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1, 1963, Abstracts, p 8M.

(18) J. F. Bunnett, C. F. Hauser, and K. V. Nahabedian, *Proc. Chem. Soc.*, 305 (1961).

(19) J. F. Stauffer and J. F. Bunnett, unpublished work; J. F. Stauffer, B.S. Thesis, Brown University, 1962.

(20) *Cf.* J. F. Bunnett and L. A. Retallick, *J. Am. Chem. Soc.*, in press.

(21) It is to be noted that mercaptide and alkoxide ions do not always exhibit the same reactivity order toward carbon.[22,23]

(22) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 271 (1963).

(23) P. E. Todesco, *Boll. Sci. Fac. Chim. Ind. Bologna*, **23**, 107 (1965).

(24) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(25) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962); *Angew. Chem.*, **74**, 731 (1962).

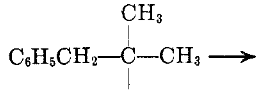
bonding of base to hydrogen in the transition state, and that alkoxide ions became relatively more reactive as transition state base-to-hydrogen bond formation became greater.

The judgment that bonding of base to hydrogen is slight in the transition states for E2 reactions of *t*-alkyl halides in alcoholic solvents stems from the theory of the variable E2 transition state.[25] In an E2 elimination, $C_\beta$–H and $C_\alpha$–X bond breaking are concerted but not necessarily synchronous. Both occur in the same step, but one may have progressed further than the other in the transition state. For the less synchronous reactions, the transition state has $C_\beta$ carbanion or $C_\alpha$ carbonium ion character according to whether $C_\beta$–H or $C_\alpha$–X rupture is the more advanced, respectively.

The character of the E2 transition state is determined by constitutional and environmental factors.[25] For reaction of a *t*-alkyl halide in methanol or ethanol, a transition state with partial $C_\alpha$ carbonium character, little $C_\beta$–H breaking and little bonding of base to $\beta$ hydrogen is postulated. This is favored by the $\alpha$-alkyl substituents, which stabilize the partial carbonium center, and by the facts that halogen atoms are rather good leaving groups and that these alcohols are rather good solvents for ions. This identification is supported by experimental observations.[7]

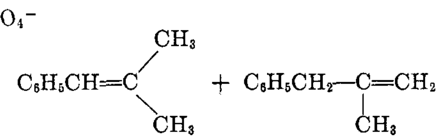
If the $RS^-/RO^-$ reactivity ratio depends on the extent of base-to-hydrogen bond formation at the transition state, this ratio should vary as the leaving group is varied in a series of E2 eliminations. As the leaving group is less prone to separate from carbon, the transition state should shift in the direction of less C–X rupture, more C–H breaking, and more base-to-hydrogen bond formation. The $RS^-/RO^-$ ratio should therefore diminish.

The present research was designed to test this hypothesis. The thioethoxide ion/methoxide ion reactivity ratio, in methanol, was determined as a function of leaving group for a series of three benzyldimethylcarbinyl derivatives of type I. The three leaving groups represented are a "good" one (chlorine), a moderately good one (dimethylsulfonio), and a poor one (methylsulfonyl).



$$C_6H_5CH_2\text{—}\overset{CH_3}{\underset{X}{C}}\text{—}CH_3 \longrightarrow$$

Ia, X = Cl
b, X = $SCH_3$
c, X = $SO_2CH_3$
d, X = $S(CH_3)_2{}^+ClO_4{}^-$



II III

## Experimental Section

**Benzyldimethylcarbinyl Ethyl Sulfide.**—A mixture of 7.4 g of benzyldimethylcarbinol, 3.50 g of 70% perchloric acid, 5.61 g of acetic anhydride, and 3.67 g of ethanethiol with enough acetic acid to make a total volume of 100 ml was combined and allowed to react according to the method of Cain, Evans, and Lee.[26] The product was isolated using their method: bp 122–124° (9 mm), $n^{25}$D 1.5302, yield 6.1 g (62%). The nmr spectrum was consistent with the structure assigned; of particular significance were sharp singlets at positions expected for the two methyl groups and the benzylic hydrogens. *Anal.* Calcd for $C_{12}H_{18}S$: C, 74.16; H, 9.33. Found:[27] C, 74.15; H, 9.10.

**Benzyldimethylcarbinyl methyl sulfide (Ib)** was similarly prepared from 37.5 g of benzylidmethylcarbinol, 10.45 ml of 70% perchloric acid, 27.75 g of acetic anhydride, 16.75 g of methanethiol, and enough acetic acid to make a total volume of 250 ml. The yield of Ib, bp 109–111° (10 mm), was 28 g (61%). The infrared spectrum showed a slight carbonyl impurity.

**Benzyldimethylcarbinyl Methyl Sulfone (Ic).**—To a mixture of 17 g of Ib and 13 ml of acetic acid, 37.4 ml of 30% hydrogen peroxide was cautiously added, and the mixture was heated for 30 min on the steam bath. The solid which formed on cooling was collected and crystallized from absolute ethanol. The sulfone (18.1 g, 90.5%) had mp 82–83° uncor. *Anal.* Calcd for $C_{11}H_{16}O_2S$: C, 62.22; H, 7.58. Found:[27] C, 62.01; H, 7.50.

**Benzyldimethylcarbinyldimethylsulfonium Perchlorate (Id).**—A mixture of 1.8 g of Ib and 2.52 g of dimethyl sulfate was allowed to stand overnight at room temperature. Water (50 ml) was added, plus enough 70% perchloric acid to dissolve all the solid which had formed. The clear solution was allowed to stand in the refrigerator. After 2 days, the crystals which had formed were collected, washed with ether (weight 2.0 g, 65%), and recrystallized from absolute ethanol. The purified salt had mp 128–130° dec uncor. *Anal.* Calcd for $C_{12}H_{19}ClO_4S$: C, 48.88; H, 6.49. Found:[27] C, 48.45; H, 6.56.

**Kinetic Measurements.**—Runs involving Ic and solvolysis studies on Id were conducted according to the procedures of Bunnett, Davis, and Tanida.[7] Reactions of Id with sodium methoxide were conducted in a similar way but in volumetric flasks, samples being taken by pipet at measured times. Reactions of Id with sodium thioethoxide were run in volumetric flasks closed with rubber caps penetrable by syringe needles, and samples were taken by syringe without opening the flasks to the air; this was to minimize air oxidation of thioethoxide to diethyl disulfide which absorbs strongly at 244 mμ.[28] In the case of the reaction between Ic and sodium thioethoxide, the slowness of the reaction made it impractical to wait for an "infinity" sample; an "infinity" absorbance value was therefore estimated from the percentage of II in the olefin product mixture as determined by gas–liquid partition chromatography.

**Product analyses** were performed by gas–liquid partition chromatography according to Bunnett, Davis, and Tanida.[7] In the case of products from reaction of Id with sodium thioethoxide, it was necessary to keep the temperature of the injection port and the column below 100° in order to avoid thermal decomposition of Ib, a major product.

**Reaction of Ic with $NaOCH_3$ in $CH_3OD$.**—Methanol-O-*d*, prepared from methyl borate,[29] was shown by its infrared spectrum to contain very little $CH_3OH$. Sodium metal (1.0 g) was allowed to react with methanol-O-*d* (25 ml) and 1.0 g of Ic was dissolved in the resulting solution. The reaction mixture was sealed in glass tubes which were heated for 10 days in a thermostat at 113.5°. The contents of the tubes were combined with water (20 ml) and extracted with cyclohexane (30-, 20-, and 20-ml portions). The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The cyclohexane was evaporated. The infrared spectrum of the residue showed broad but not intense absorption at *ca.* 2200 $cm^{-1}$, attributed to C–D stretching, but was otherwise indistinguishable from the spectrum of an ordinary olefin mixture. A sample of the product was also examined in the mass spectrometer (results are described in text).

**Kinetics of Isomerization of III to II.**[30]—A mixture of II and III, from sulfuric acid dehydration of benzyldimethylcarbinol, was separated into its components by glpc. A methanolic solution 1.20 *M* in sodium methoxide and $5.2 \times 10^{-4}$ *M* in III was dispensed into ampoules which were sealed and immersed in the thermostat at 114°. The progress of the reaction was followed photometrically at 244 mμ. The "infinity"

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[26] M. E. Cain, M. B. Evans, and D. F. Lee, *J. Chem. Soc.*, 1694 (1962).

[27] Analysis was by Micro-Tech Laboratories, Skokie, Ill.

[28] R. C. Passerini, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Ltd., London, 1961, p 57.

[29] J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

[30] We are indebted to Dr. Claude Bernasconi for performing this experiment.

TABLE I

KINETICS OF METHANOLYSIS OF Id, AND OF REACTIONS OF Ic AND Id WITH $NaOCH_3$ OR $NaSC_2H_5$ IN METHANOL

| Leaving group | Basic reagent and concn, *M* | Other substance and concn, *M* | Temp, °C | $10^5k_\psi$, $sec^{-1}$ | $10^3k_{tot}$,[a] $M^{-1}$ $sec^{-1}$ | Product compn, %: II (photometric) | II (glpc) | III (glpc) | Ib (glpc) | $10^3k_{II}$, $M^{-1}$ $sec^{-1}$ | $10^3k_{III}$, $M^{-1}$ $sec^{-1}$ | $10^3k_{Ib}$, $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S(CH_3)_2^+$ | | | 51.7 | 1.72 | | 18.1 | | | | | | |
| | | | 64.0 | 9.40 | | 16.6 | | | | | | |
| | | | 76.8 | 62.8 | | 16.8 | | | | | | |
| | | $NaClO_4$, 0.40 | 51.5 | 1.66 | | 14.1 | | | | | | |
| | | NaBr, 0.43 | 51.5 | 2.47 | | 33.8 | | | | | | |
| | | 0.84 | 51.5 | 3.18 | | 39.6 | | | | | | |
| | $NaOCH_3$, 0.030 | | 29.5 | 3.00 | 2.11 | 69.2 | 70.3 | 29.7 | | 1.5 | 0.6 | |
| | 0.030 | NaBr, 0.033 | 29.5 | 2.11 | | 69.2 | | | | | | |
| | 0.030 | 0.065 | 29.5 | 1.70 | | 66.2 | | | | | | |
| | 0.090 | | 29.5 | 6.60 | 2.67 | 67.2 | 70.3 | 29.7 | | 1.9 | 0.8 | |
| | 0.090 | | 36.4 | 15.4 | 6.43 | 66.1 | 69.0 | 31.0 | | 4.4 | 2.0 | |
| | 0.045 | | 42.6 | 24.4 | 14.3 | 68.6 | 68.1 | 31.9 | | 9.7 | 4.6 | |
| | $NaSC_2H_5$, 0.030 | $C_2H_5SH$, 0.015 | 29.5 | 35.8 | 25.8 | 7.6 | | | | 1.4 | 0.6 | 23.8 |
| | 0.045 | 0.022 | 29.5 | 40.4 | 23.1 | 6.3 | 5.6[b] | 2.2[b] | 92.2[b] | 1.3 | 0.5 | 21.3 |
| | 0.046 | 0.022 | 29.5 | 42.7 | 23.9 | 5.9 | | | | 1.3 | 0.5 | 22.1 |
| | 0.046 | 0.022 | 36.4 | 60.9 | 35.2 | 7.5 | 4.8 | 2.2 | 93.0 | 1.8 | 0.7 | 32.8 |
| | 0.045 | 0.022 | 42.6 | 176. | 106 | *c* | 5.2 | 1.5 | 93.3 | 5.3 | 2.1 | 98.5 |
| $SO_2CH_3$ | $NaOCH_3$, 1.20 | | 113.9 | 0.54 | 0.0045 | 93.5[d] | 94.5[d] | 5.5[d] | | 0.0042[d] | 0.0003[d] | |
| | $NaSC_2H_5$, 1.00 | $C_2H_5SH$, 0.49 | 113.9 | 0.02 | 0.0002 | *ca.* 100 | | | | 0.0002 | | |

[a] Corrected to zero ionic strength. [b] Products from a run with 0.44 *M* $NaSC_2H_5$ and 0.19 *M* $C_2H_5SH$. [c] Not recorded. [d] See text concerning possible error in these values.

absorbance used for computation was calculated from the extinction coefficient of II on the assumption of complete isomerization to II. First-order kinetics were observed; the pseudo-first-order coefficient was $2.8 \times 10^{-6}$ $sec^{-1}$

## Results

Our rate measurements, with associated product analysis, are summarized in Table I. These concern only substrates Ic and Id. Data concerning reactions of Ia are available from Bunnett, Davis, and Tanida.[7]

**Elimination from Sulfonium Salt Id.**—Three experiments in which Id was allowed to react with 0.03 *M* sodium methoxide showed that the over-all reaction rate is depressed by addition of sodium bromide, an unreactive salt under these conditions. Inasmuch as reaction between an anion and a cation is under study, it was to be expected that the rate coefficient would diminish with increase of ionic strength. The Brønsted–Bjerrum–Scatchard equation may be put in the form

$$\log k = \log k_0 + B\sqrt{\mu}/(DT)^{3/2}$$

where *D* is the dielectric constant, *T* the absolute temperature, $\mu$ the ionic strength, and *B* a composite parameter.[31] Log $k_\psi$ for these three runs was indeed linear with $\sqrt{\mu}$, as shown in Figure 1. The intercept represents the pseudo-first-order rate coefficient corrected to zero ionic strength.

From the slope in Figure 1 (−1.87), the temperature and the dielectric constant of methanol at 29.5°, the parameter B was evaluated. The magnitude of $B/(DT)^{3/2}$ was then computed for other temperatures, and all the measured $k_\psi$ values for reactions of Id with methoxide or thioethoxide were corrected to zero ionic strength. Division by the methoxide or thioethoxide concentration gave $k_{tot}$, the over-all second-order rate coefficient as listed in Table I. $k_{tot}$ was dissected into $k_{II}$, $k_{III}$, and $k_{Ib}$ in proportion to the yields of these products.

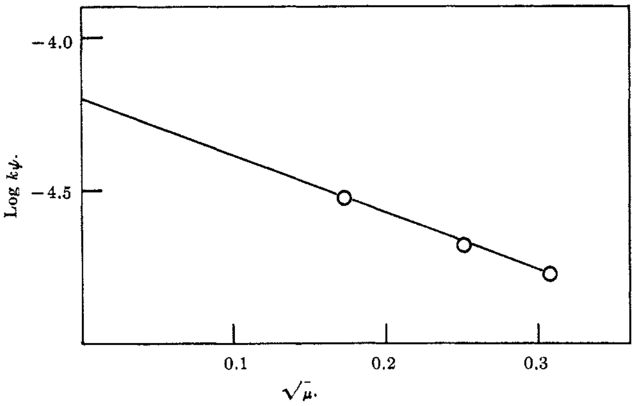

Figure 1.—Relationship of log $k_\psi$ to square root of ionic strength, for reaction of Id with $NaOCH_3$ at 29.5°.

The rate of solvolysis of Id was determined at three temperatures (the first three experiments in Table I). The (extrapolated) solvolysis rates at the temperatures used for reactions of Id with methoxide and thioethoxide were negligibly small compared with the bimolecular elimination rates. Although sodium perchlorate slightly depressed the solvolysis rate, with little change in the yield of II, sodium bromide considerably accelerated decomposition of Id and increased the yield of II. This indicates that bromide ion acted as a nucleophile toward Id, at least in part to initiate elimination. Similar effects have been described by Cocivera and Winstein.[32] Acceleration of sulfonium ion decomposition in aqueous ethanol by added lithium halide salts has been reported by Hyne and co-workers.[33]

Reaction of Id with sodium thioethoxide occurred more than 90% by displacement on methyl carbon, forming Ib and (presumably) ethyl methyl sulfide. It is known that mercaptide ions are very reactive in SN2 displacements with sulfonium salts.[34] It was

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[31] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp 124–127.

[32] M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963).

[33] J. B. Hyne and J. W. Abrell, *Can. J. Chem.*, **39**, 1657 (1961); J. B. Hyne and J. H. Jensen, *ibid.*, **40**, 1394 (1962).

[34] A. Luttringhaus and H. Machatzke, *Ann.*, **671**, 165 (1964).

TABLE II

SUMMARY OF KINETIC DATA

| Reaction | $k$, $M^{-1}$ sec$^{-1}$ | $\Delta H^*$,[a] kcal | $\Delta S^*$, eu[a] | $k_{RS^-}/k_{RO^-}$ |
|---|---|---|---|---|
| Reactions of sulfonium salt Id | | | | |
| Solvolysis | $4.4 \times 10^{-7}$[b] (29.5°) | $31.7 \pm 1.3$ | $+17 \pm 4$ | |
| Id + $NaOCH_3 \longrightarrow$ II | $1.7 \times 10^{-3}$ (29.5°) | $25 \pm 2$ | $+10 \pm 7$ | |
| Id + $NaOCH_3 \longrightarrow$ III | $0.7 \times 10^{-3}$ (29.5°) | $27 \pm 2$ | $+6 \pm 8$ | |
| Id + $NaSC_2H_5 \longrightarrow$ II | $1.3 \times 10^{-3}$ (29.5°) | $17 \pm 4$ | $-14 \pm 12$ | 0.8 |
| Id + $NaSC_2H_5 \longrightarrow$ III | $0.5 \times 10^{-3}$ (29.5°) | $17 \pm 4$ | $-17 \pm 13$ | 0.7 |
| Id + $NaSC_2H_5 \longrightarrow$ Ib | $2.24 \times 10^{-2}$ (29.5°) | $19 \pm 3$ | $-4 \pm 11$ | |
| Reactions of sulfone Ic | | | | |
| Ic + $NaOCH_3 \longrightarrow$ II | $4.2 \times 10^{-6}$[c] (113.9°) | | | |
| Ic + $NaOCH_3 \longrightarrow$ III | $3 \times 10^{-7}$[c] (113.9°) | | | |
| Ic + $NaSC_2H_5 \longrightarrow$ II | $2 \times 10^{-7}$ (113.9°) | | | 0.05 |
| Reactions of chloride Ia[d] | | | | |
| Ia + $NaOCH_3 \longrightarrow$ II | $1.52 \times 10^{-4}$ (75.8°) | | | |
| Ia + $NaOCH_3 \longrightarrow$ III | $0.38 \times 10^{-4}$ (75.8°) | | | |
| Ia[d] + $NaSC_2H_5 \longrightarrow$ II | $9.85 \times 10^{-4}$ (75.8°) | | | 6.5 |
| Ia[d] + $NaSC_2H_5 \longrightarrow$ III | $4.35 \times 10^{-4}$ (75.8°) | | | 11.4 |

[a] Uncertainties shown in $\Delta H^*$ and $\Delta S^*$ are standard deviations, based on standard deviations in slopes of Arrhenius plots. [b] Units of sec$^{-1}$. [c] See text concerning possible error in these values. [d] All data concerning Ia are from ref 7.

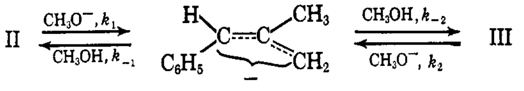
nevertheless possible to determine the yields of olefins II and III with accuracy.

Arrhenius plots were constructed for the several reactions of Id, with use of the dissected rate coefficients listed in Table I. These plots, except that for solvolysis, showed considerable scatter. Slopes and standard deviations of slopes were computed by linear regression analysis. The resulting activation parameters, calculated by standard expressions, are listed in Table II.[35]

**Elimination from Sulfone Ic.**—Inasmuch as the methylsulfonyl group is a poor leaving group and rather strongly electron attracting, it was conceivable that elimination occurred by the carbanion mechanism. If the conceivable intermediate carbanion (formed by removal of a proton from the benzylic position) reverted to Id much more frequently than it progressed to olefin II, reaction in $CH_3OD$ solution ought to form Ic doubly deuterated at the benzylic position and ultimately II containing one deuterium atom per molecule. (Carbanion formation at one of the terminal methyl carbon atoms is much less probable.) In this event, the olefin mixture formed by elimination in methanol-O-*d* showed some C–D absorption in the infrared. Its mass spectrum indicated 38% undeuterated $C_{10}H_{12}$, 39% monodeuteration ($C_{18}H_{11}D$), 18% dideuteration, and 4% trideuteration.[36]

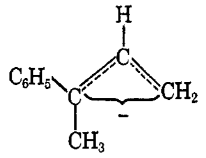
It is probable, however, that deuteration occurred by isotopic exchange in the olefin products rather than in Ic before elimination. The rate of isomerization of olefin III to the equilibrium mixture of II and III was determined under the conditions (1.2 *M* $NaOCH_3$, 114°) of the elimination run. The pseudo-first-order rate coefficient, $2.8 \times 10^{-6}$ sec$^{-1}$, was dissected into forward and reverse coefficients with reference to the composition of the equilibrium mixture (about 95% II and 5% III). The coefficient for isomerization of II to III was thereby estimated to be about $1.4 \times 10^{-7}$ sec$^{-1}$, corresponding to a half-life of about 1400 hr. For comparison, the duration of the elimination experiment in $CH_3OD$ was about 240 hr.

Isomerization doubtless occurs *via* the allylic anion, IV. The second-order rate coefficient for isomerization of II to III is given by $k_1k_{-2}/(k_{-1} + k_{-2})$.[37] If the "collapse ratio," $k_{-2}/k_{-1}$, is small, many events of reversion of IV to II occur for each progression of IV to III. In such a case the exchange rate (in $CH_3OD$) would be much greater than the isomerization rate.



IV

The collapse ratio is not known for IV. For V, an isomer of IV, the collapse ratio is about 20 in favor of the conjugated olefin analogous to II.[37] A strong preference for IV to revert to II therefore seems probable in the present system.



V

Moreover, the distribution of deuterium in the olefins formed in $CH_3OD$ is in better accord with exchange following elimination. Had exchange occurred before and not after deuteration, the II formed should have contained no more than one deuterium and the III (only about 5% of the mixture) not more than two deuteriums.

Thus formation of deuterated olefins in $CH_3OD$ can be readily accounted for in terms of exchange after elimination. Indeed, such an interpretation is preferred. The occurrence of a small amount of exchange prior to elimination is, however, not excluded, nor do these experiments in themselves exclude the pos-

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(35) Possible reasons for the relatively large standard deviations in activation parameters are (a) the small temperature range (13.1°) covered by the data; (b) the possibility of error in the procedures used to correct rate coefficients to zero ionic strength; and (c) in the case of reactions with thioethoxide ion, the fact that small absolute errors in determining the percentages of II and III would constitute large relative errors owing to the small olefin yields.

(36) We are indebted to Dr. G. G. Volpi, Mass Spectrometry Laboratory, National Council for Nuclear Energy, Rome, Italy, for the mass spectrometric analysis and interpretation.

(37) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 204–210.

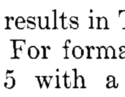
sibility that the whole elimination reaction goes *via* carbanion intermediates which expel the leaving group much faster than they revert to Ic. However, the latter possibility is most unlikely when the leaving group is notably loathe to depart from carbon.

The pseudo-first-order rate coefficient for methoxide-induced elimination from Ic is only about twice that for equilibration of olefins II and III under the same conditions. It follows that the "infihity" product composition from Ic must approximate the thermodynamically controlled olefin ratio. Therefore $k_{\mathrm{II}}$ and $k_{\mathrm{III}}$ as listed in Tables I and II, which are based on the "infinity" olefin composition, are in error because they ought to be based on the kinetic olefin ratio. However, that the thermodynamic ratio does not greatly differ from the kinetic ratio is suggested by the fact that the plot of log $(A_\infty - A_t)$ *vs.* time (ten points) defined an excellent straight line through 79% of the reaction. The error in $k_{\mathrm{II}}$ is assuredly not more than 20%, but that in $k_{\mathrm{III}}$ may be larger. The conclusions drawn from these rate coefficients (*vide infra*) are not affected by the uncertainty in these values.

## Discussion

In the introduction, the hypothesis was formulated that, if mercaptide-induced eliminations are normal E2 reactions and if the mercaptide/alkoxide reactivity ratio depends on the degree of bonding of base to hydrogen in the transition state, the thioethoxide/methoxide ratio should diminish as the leaving group becomes "poorer." The results in Table II are in accord with this hypothesis. For formation of olefin II, the RS$^-$/RO$^-$ ratio is 6.5 with a good leaving group (chlorine), 0.8 with a moderately good leaving group (dimethylsulfonio), and 0.05 with a very poor leaving group (methylsulfonyl). For formation of III, the trend is the same although a ratio is not available for Ic.

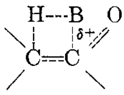
Let us seek to account for these results in terms of the competing hypothesis, that there is covalent interaction of the nucleophile with both $H_\beta$ and $C_\alpha$ in the transition state.[38] If the character of the transition state varies with the proclivity of the leaving group to separate from carbon, there should be considerable carbonium character at $C_\alpha$ when the leaving group is chlorine, less when it is dimethylsulfonio, and virtually none when it is methylsulfonyl. Partial carbonium character implies a partially developed vacant p orbital which should be available for overlap with an occupied orbital of an attacking nucleophile. To the extent that such overlap occurs, the elimination transition state might be pictured as VI, in which B is the nucleophile (base). Such overlap would be expected to be greater the greater the carbonium character at $C_\alpha$ and thus greater the "better" the leaving group. If a mercaptide ion can interact with $C_\alpha$ better than an alkoxide ion in such a transition state, the mercaptide/alkoxide reactivity ratio should increase the "better" the leaving group, as observed in our experiments. Thus the hypothesis of partial covalent interaction with carbon in the elimination transition state would also seem to be compatible with the dependence of the RS$^-$/RO$^-$ ratio on leaving group.



VI

However, that hypothesis remains unsatisfying for two principal reasons. First, if mercaptide ions are especially reactive because they interact covalently with carbon in the transition states for elimination from *t*-alkyl halides, it is difficult to understand why *t*-alkyl sulfides are not formed in appreciable amounts as products. This argument has been presented before,[7] and it has been criticized as "fallacious" by Kevill, Coppens, and Cromwell.[14] Although it is not a compelling argument against the hypothesis of partial covalent interaction with $C_\alpha$, it is not fallacious. The virtual absence of mercaptide substitution products remains a difficult experimental fact for that hypothesis to accommodate.

Secondly, if covalent interaction with an adjacent carbon atom of partial carbonium character is principally responsible for the high mercaptide/alkoxide reactivity ratios with *t*-alkyl halides, similarly high ratios ought also to be observed in proton abstraction from the α carbon of ketones. The carbonyl carbon has partial carbonium character, and covalent interaction of nucleophiles jointly with the carbonyl and α carbons is held to be responsible for the high reactivity of α-chloroketones with nucleophiles.[39] For proton abstraction from the α carbon, a transition state such as VII is conceivable. However, mercaptide ions are distinctly less effective than alkoxide ions in generating enolate ions from ketones.[19,20] Thus a prediction based on a short and direct extension of the hypothesis of partial covalent interaction of nucleophile (base) with $C_\alpha$ in the elimination transition state fails of experimental fulfillment.



VII

The hypotheses that the mercaptide-induced eliminations are normal E2 reactions and that mercaptide ions are superior nucleophiles toward hydrogen when the nucleophile (base) is but slightly bound to hydrogen in the transition state give, over-all, a better account of the facts.

Let us inquire why mercaptide ions are especially reactive toward hydrogen when the transition state is of this character. Hudson's theory of nucleophilic reactivity,[40] though incomplete, is nevertheless illuminating when applied to the present question. Hudson considers three energetic factors to be of special importance in determining nucleophilic reactivity. Two are "cost" factors: the energy which must be supplied to (partially) desolvate the nucleophile and to (partially) remove an electron from an outer-shell orbital. These "costs" are both expected to be lower for nucleophiles of high polarizability, such as mer-

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(38) *Cf.* ref 10, footnote 9.

(39) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

(40) R. F. Hudson, *Chimia* (Aarau), **16**, 173 (1962); see also the review of Bunnett.[22]

captide ions, than for low polarizability, high basicity nucleophiles such as methoxide ion. The third is a "return" factor: the energy released by (partial) bond formation between the nucleophile and the electrophilic center. The magnitude of the "return" will depend on the strength of the bond being formed and on the extent of its formation in the transition state.

Inasmuch as the bond dissociation energy of the O–H is considerably greater than that of the S–H bond,[41] the third factor favors alkoxide over mercaptide ions when there is a large degree of bonding of base to hydrogen in the transition state. However, this is much less significant when there is but a small degree of bonding of base to hydrogen. In such cases, the smaller energetic cost of desolvating mercaptide ions and of partially removing electrons from outer-shell orbitals should be relatively more important and perhaps predominant. Evidently these factors are predominant in the reactions of *t*-alkyl halides with mercaptide and alkoxide ions in alcoholic solvents.

Table II provides experimental evidence that more desolvation of methoxide than of thioethoxide ion occurs in forming the E2 transition state. Although the experimental uncertainty in the entropies of activation is rather high,[35] it is nevertheless clear that this parameter is more positive for the methoxide than for the thioethoxide reactions. Release of solvent molecules in forming the transition state tends to raise the entropy of activation.

Recently, England and McLennan[42,43] have conducted an independent series of investigations of the variation of the mercaptide/alkoxide reactivity ratio as the character of the transition state varies in E2 eliminations. Their conclusions are in excellent agreement with those drawn in the present discussion.

(41) H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 287 (1963)

(42) B. D. England and D. J. McLennan, *J. Chem. Soc.*, (B), 696 (1966).

(43) D. J. McLennan, *ibid.*, (B), 705, 709 (1966).

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# The Electrochemical Oxidation of Cyclooctatetraene in Acetic Acid Containing Acetate Ion

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*Received August 12, 1966*

The electrochemical oxidation of cyclooctatetraene in acetic acid containing acetate ion has been studied at both constant anode potential and constant current. With a platinum anode two product fractions were obtained. The first was shown to be a mixture of *cis*- and *trans*-7-methyl-8-acetoxybicyclo[4.2.0]octa-2,4-diene. The larger second fraction was shown to be a mixture of *cis*- and *trans*-bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetate and cycloheptatrienecarboxaldehyde diacetate. With a carbon anode only the latter of the above two product mixtures was obtained. The mechanisms of these reactions have been discussed. The cation radical, resulting from a one-electron transfer, and the planar cyclooctatriene dication are possible intermediates.

Previous studies of the anodic acetoxylation of organic compounds in acetic acid containing acetate ion[1-4] have demonstrated that this reaction commonly occurs *via* an initial two-electron transfer from the organic substrate to form an electrophilic species. The acetoxylated products are formed from ionic intermediates and are not the result of a homolytic reaction between an anodically generated acetoxy radical and the substrate. This interpretation is supported by polarographic measurements,[1,2] by the products formed by electrolysis at controlled potential (cpe),[1,2] and by studies of the rates of gas formation at the anode.[3,4] This mechanism has also been proposed by Salzberg and co-workers,[5,6] by Bonner and Mango,[7] and by Steuber and Dimroth[8] for anodic acetoxylation, by Parker and Burgert[9] for anodic cyanation, and by Schmidt and Meinert[10] for anodic fluorination.

The electrochemical behavior of cyclooctatetraene (COT) is of particular interest, since either a two-electron reduction or a two-electron oxidation offers the possibility of converting COT from its stable, "tub" conformation into a molecule having a planar, regular, octagonal conformation, $4n + 2$ $\pi$ electrons, and aromatic character.[11] This possibility on reduction has been fully realized.[12,13] Polarography in anhydrous dimethyl sulfoxide or N,N-dimethylformamide (DMF) shows that COT is reduced in two one-electron steps, the intermediate monoanion radical being identified by its esr spectrum during controlled-potential electrolysis in DMF. With proton donors present the two cathodic waves coalesce into a single two-electron wave. Preparative experiments[13]

(1) L. Eberson and K. Nyberg, *Acta Chem. Scand.*, **18**, 1568 (1964).

(2) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

(3) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 4139 (1964).

(4) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

(5) M. Leung, J. Herz, and H. W. Salzberg, *ibid.*, **30**, 310 (1965).

(6) H. W. Salzberg and M. Leung, *ibid.*, **30**, 2873 (1965).

(7) F. D. Mango and W. H. Bonner, *ibid.*, **29**, 1367 (1964).

(8) F. W. Steuber and K. Dimroth, *Chem. Ber.*, **99**, 258 (1966).

(9) V. D. Parker and B. E. Burgert, *Tetrahedron Letters*, 4065 (1965).

(10) H. Schmidt and H. Meinert, *Angew. Chem.*, **72**, 109 (1960).

(11) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(12) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

(13) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87**, 2336 (1965).