B. Reactions in benzene were performed analogously. After the appropriate hours shown (Table I), methanol (10 ml) was added to the reaction mixture, and the mixture was treated in the same manner as the reaction in acetonitrile for the isolation of the products.

C. Reaction in Benzene–Methanol.—A solution of **6a** (1.99 g, 10 mmol) in benzene–methanol (8.4:1, 30 ml) was added to a boiling solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) and the resultant solution was refluxed for 2 hr. The mixture was concentrated by rotary evaporation, and the residue was treated in the same manner as the reaction in acetonitrile for the isolation of the products.

In the Presence of Catalyst. A. Reaction in Acetonitrile.—To a solution of **2** (2.62 g, 10 mmol) in acetonitrile (50 ml) were added, with stirring, 5 drops of triethylamine[4] and then a solution of **6a** (1.99 g, 10 mmol) in acetonitrile (30 ml). After 2 hr, methanol (10 ml) was added to the mixture. The mixture was concentrated by rotary evaporation, and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.2 g, 91%). In place of triethylamine as the catalyst, aqueous potassium cyanide (5 drops of a 33% solution) was effecively used in each 10-mmol-scale reaction.

B. Reaction in Benzene.—To a solution of **2** (2.62 g, 10 mmol) in benzene (40 ml) were added, with stirring at room temperature, 5 drops of triethylamine and then a solution of **6a** (1.99 g, 10 mmol) in benzene (30 ml). After 2 hr, methanol (10 ml) was added to the mixture. The mixture was concentrated by rotary evaporation and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.35 g, 94%).

C. Reaction in Benzene–Methanol.—To a solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) were added, with stirring at room temperature, 5 drops of triethylamine and then a solution of **6a** (1.99 g, 10 mmol) in benzene–methanol (8.4:1, 30 ml). After 2 hr, the resultant mixture was concentrated by rotary evaporation and the residue was treated with tetrahydrofuran (20 ml). The crystalline **7a** was collected by filtration (4.25 g, 92%). In place of triethylamine as catalyst, pyridine (5 drops) was effectively used in a 10-mmol-scale reaction.

Reaction in the Presence of (2-Oxo-2-phenylethyl)pyridinium Bromide (9).—To a solution of **2** (2.62 g, 10 mmol) in benzene–methanol (8.4:1, 40 ml) were added, with stirring at room temperature, 0.3 g (1 mmol) of (2-oxo-2-phenylethyl)pyridinium bromide (**9**), mp 191.5–192° (lit.[13] 199–200°), and then a solution of **6a** (1.99 g, 10 mmol) in the mixed solvent (30 ml). After 2 hr, the mixture was concentrated by rotary evaporation and the residue was treated in a same manner as in the reaction in acetonitrile for the isolation of the products.

Registry No.—**2**, 603-35-0; **6a**, 70-11-1; **6b**, 99-81-0; **6c**, 99-73-0; **6d**, 619-41-0; **6e**, 2632-13-5; **6f**, 2114-00-3; **6g**, 532-27-4; **7b**, 17730-93-7.

[13] J. W. Baker, *J. Chem. Soc.*, 1148 (1932).

The Thermal Decomposition of Solid Benzyldimethylsulfonium Salts. Significance of the Kinetic Behavior

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The kinetics of thermal decomposition of solid benzyldimethylsulfonium salts are compared with predictions derived from a theoretical model, construction of which assumes that each reacting particle approximates a sphere or regular polyhedron, that reaction takes place at the surface only, and that the distribution of particle sizes is accurately expressed by a simple exponential equation. Kinetic orders based on the "log normal" distribution law (eq 5) are constant through at least 95% reaction and best fit the experimental values.

In an earlier paper[2] it was suggested that a cubic or spherical particle or a uniform aggregate of such particles decomposing at the surface to give volatile products should obey two-thirds-order kinetics (eq 1). The

$$\frac{dw}{dt} = -kw^{2/3} \tag{1}$$

kinetics of thermal decomposition of solid benzyldimethylsulfonium salts vary from less than two-thirds order to greater than first order for pulverized and unpulverized samples (Table I). Decomposition of a pulverized sample incorporating a wide range of particle sizes might not be expected to follow eq 1, and evidence presented here argues that orders higher than two-thirds are to be anticipated.

TABLE I

REACTION ORDERS FOR THERMAL DECOMPOSITION OF SOLID $RC_6H_4CH_2S(CH_3)_2X$[a]

1–6a, X = Cl
b, X = Br
c, X = I

		X		
Compd	R	Cl[b]	Br	I
1	H	0.7–0.9	0.7–0.9	0.6–0.7
2	p-CH_3	0.7–0.8	0.9–1.1	1.2–1.3
3	p-Cl	0.6–0.7	1.0–1.2	1.3–1.5
4	p-NO_2	0.8	0.67	1.0 (88°)
				0.9 (93°)
				0.7 (98°)
5	m-NO_2	0.7	0.8–1.2	0.9–1.0
6	p-CH_3O	0.9 (78°)	0.8 (78°)	0.6 (60°)
		0.6 (83°)	0.5 (83°)	0.5 (65°)
			0.4 (88°)	0.5 (70°)

[a] Reaction orders are evaluated by fitting to eq 6 the kinetic data obtained as described in ref 2. [b] Chloride samples were not pulverized.

A number of equations have been proposed to describe the particle size distribution of milled solids. One of the earliest was suggested by Heywood,[3] who assumed that the number of particles of diameter x would obey eq 2, and that the particle weight distribution would therefore follow eq 3.

$$\frac{dN}{dx} = be^{-bx} \tag{2}$$

$$\frac{dG}{dx} = kx^3e^{-bx} \tag{3}$$

Later, Rosin and Rammler developed a modified form of eq 3 which could be applied to mill products of a wide variety of

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[2] W. D. Burrows and J. H. Cornell, *J. Org. Chem.*, **32**, 3840 (1967).

[3] H. Heywood, *J. Inst. Fuel*, **6**, 241 (1933).

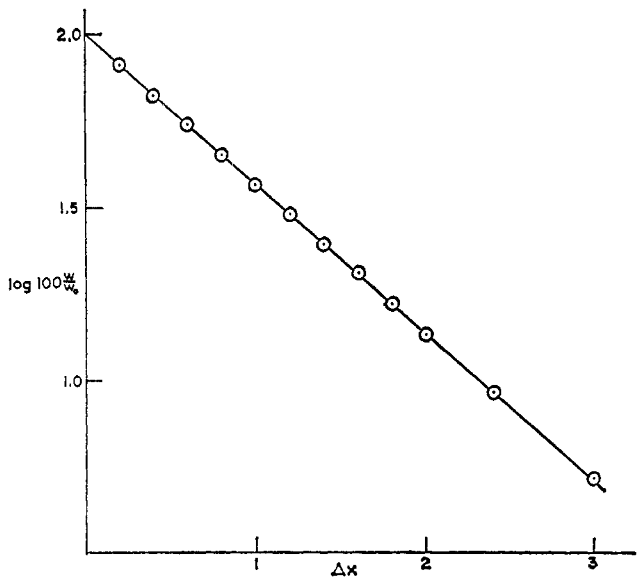

Figure 1.—Model decomposition reaction based on particle size distribution (eq 3).

coals and ceramic materials (eq 4).[4] Values of n, a measure of particle size uniformity, were determined to

$$\frac{dG}{dx} = kx^{n-1}e^{-xn} \qquad (4)$$

range from *ca.* 1 to 1.4. Equation 4 is subject to the same theoretical objections[5] as eq 3 at the limits of x, but Rosin and Rammler claim that sieve analyses establish an accuracy of 1–2% for particle sizes of 10–200 μ. Recent consensus favors the "log normal" distribution law[6] (eq 5; σ here is the geometric standard

$$\frac{dG}{dx} = kx^2 \exp(-{}^1/_2 \log^2 x/\log^2 \sigma] \qquad (5)$$

deviation by weight), which gives greater relative importance to particles with diameters well above average and lesser importance to particles of diminishing diameter than does eq 4.[7]

Having selected a distribution function it is simple in principle to determine the kinetics of weight loss for a model system, assuming that the particles approximate spheres or regular polyhedra and that decomposition takes place at the surface only, *i.e.*, that eq 1 is valid for each particle. Heywood's formulation leads to a virtually perfect first-order plot out to 95% reaction (Figure 1). Rates derived from the equation of Rosin and Rammler have been evaluated for five n values from 1 to 2. The highest value gives a good first-order plot (slightly serpentine) to 98% reaction, while lesser n values lead to kinetic orders greater than one, although there is a tendency in all cases to first-order kinetics as the model reaction proceeds (Figure 2). Thus acceptance of the exponential law of Rosin and Rammler and their limits on n values requires that no reaction for which eq 1 is valid has a kinetic order less than one. For log normal plots σ is an inverse measure of particle size uniformity. Gallagher, who has devised a computer program utilizing the log normal equation to evaluate the effect of particle size distribution on the kinetics of diffusion reactions in powders, reports commercially measured σ values of 1 (perfect uniformity) to 4.[8] This corresponds to a much wider range than the equivalent n values of Rosin and Rammler. For the present work five values of σ from 1.5 to 3 have been selected as typical, and are found in each case to lead to a reaction order constant through 95% weight loss (eq 6 and Figure 3, *e.g.*).

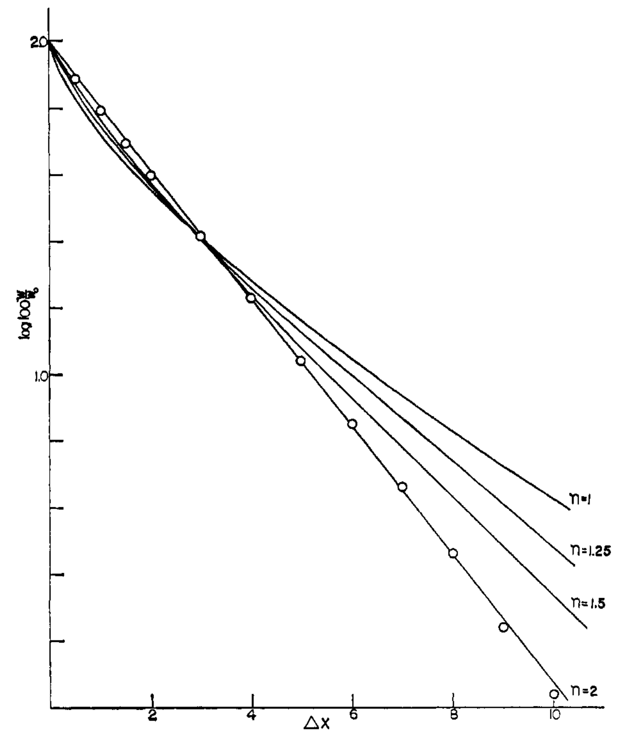

Figure 2.—Model decomposition reaction based on particle size distribution (eq 4).

$$\frac{dw}{dt} = -kw^m \qquad (6)$$

σ:	1.5	1.6	2.0	2.5	3.0
m:	0.9	1.0	1.2	1.4	1.6

Comparing theoretical and observed kinetics, it is readily seen that the log normal distribution gives a better fit than the equation of Rosin and Rammler, even when rate plots derived from the latter are corrected for the fact that in actual kinetic runs *ca.* 30% of the material was allowed to decompose before measurements of weight loss were begun. Discussion for the rest of this exposition will therefore concern the model derived from eq 1 and 5, but whether one employs the Heywood, log normal, or Rosin and Rammler distribution law it appears unlikely that the model can account for kinetic orders less than one.[9,10] There are

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[4] P. Rosin and E. Rammler, *J. Inst. Fuel.*, **7**, 29 (1933).

[5] R. R. Irani and C. F. Callis, "Particle Size: Measurement, Interpretation and Application," John Wiley and Sons, Inc., New York, N. Y., 1963, p 39.

[6] G. Herdan, "Small Particle Statistics," Butterworth Ltd., London, 1960, p 81 ff.

[7] Because actual particle diameters are not relevant to this study, eq 4 and 5 are presented here in simplified form.

[8] K. J. Gallagher, 5th International Symposium on the Reactivity of Solids, G.-M. Schwab, Ed., Elsevier Publishing Co., New York, N. Y., 1965, p 192.

[9] Of course no particle size distribution can account for kinetic orders less than two-thirds, and most certainly the precise two-thirds-order dependence of the decomposition of p-nitrobenzyldimethylsulfonium bromide[2] is an artifact.

[10] Because the mathematical treatment becomes cumbersome and imprecise with σ values exceeding 3, it has not been determined whether, as seems likely, higher reaction orders can be explained in terms of particle size distribution. A. K. Galwey [*J. Chem. Soc.*, 5433 (1965); *ibid.*, *Sect. A*, 87 (1966)] has observed second- and third-order processes in the thermal decomposition of metal salts of mellitic acid.

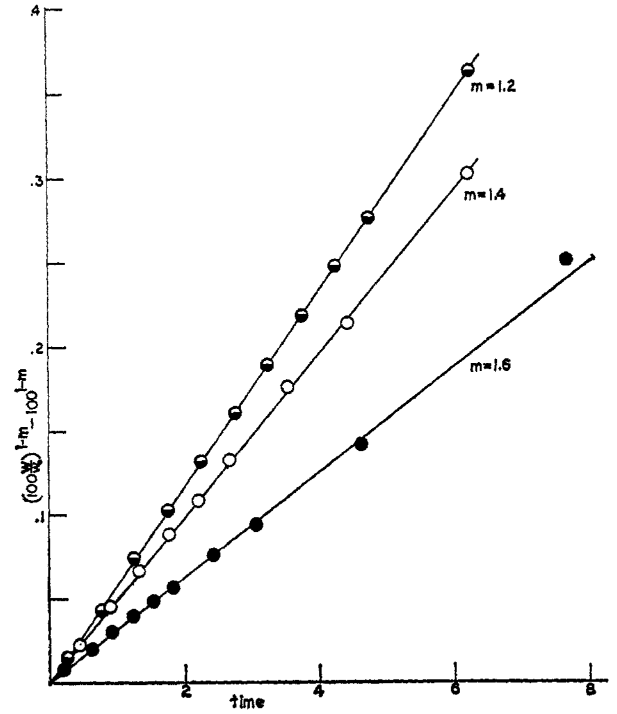

Figure 3.—Model decomposition reaction based on particle size distribution [eq 6 with σ = 2 (m = 1.2), σ = 2.5 (m = 1.4), and σ = 3 (m = 1.6)].

substantial differences in the observed kinetic orders and, although it is possible to correlate these differences with σ values in most cases, it seems reasonable to suppose that similar materials pulverized under identical conditions will not differ greatly in particle size distribution. Rather, differences in kinetic order may more accurately reflect differences in structure. For the methyl-, nitro-, and chlorobenzyl derivatives there is a trend to increasing kinetic order in going from chloride to bromide to iodide, in agreement with the earlier observation that decomposition of most iodides is strongly accelerated by pulverizing, bromide decomposition is moderately accelerated, and chloride decomposition is nearly unchanged. This was explained by invoking a two-step reaction mechanism. In the first step (eq 7) the salt dissociates reversibly to benzyl halide and dimethyl sulfide, and in the second step (eq 8) the products diffuse irreversibly from the

$$[\mathrm{ArCH_2S(CH_3)_2X}]_{\text{crystal}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{ArCH_2X + (CH_3)_2S}]_{\text{crystal}} \quad (7)$$

$$[\mathrm{ArCH_2X + (CH_3)_2S}]_{\text{crystal}} \xrightarrow{k_2} \mathrm{ArCH_2X + (CH_3)_2S} \quad (8)$$

crystal lattice. Re-formation of the sulfonium salt is more probable for benzyl iodide than benzyl chloride, and diffusion of benzyl chloride is probably faster. Thus pulverizing the crystal greatly increases k_2/k_{-1} for the iodide, but this ratio is not rate limiting for the chloride. It is not surprising that the mathematical model better describes the iodides than the bromides or chlorides, for a solid material decomposing from within as well as at the surface would not be expected to obey eq 1. The internal reaction, which results in an increase in surface area and shattering of larger crystals from internal strain, is responsible for the induction period observed particularly in the decomposition of unpulverized chlorides. Lattice defects caused by departure of the volatile products present a special case of nucleation, commonly observed in the thermal decomposition of solid metal salts (such as silver azide), to which the characteristic S-shaped reaction curves are attributed.[11]

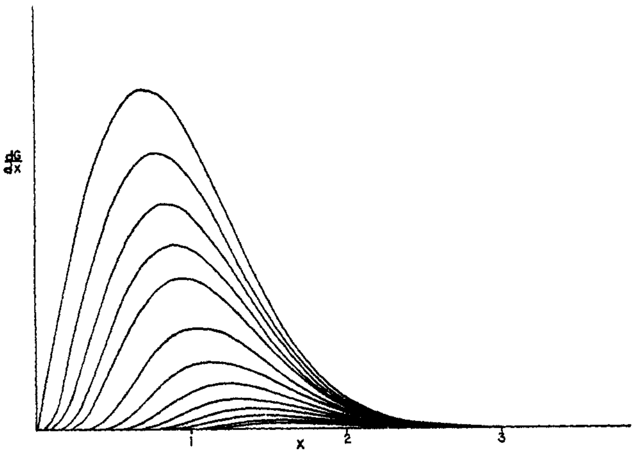

Figure 4.—Frequency functions for a decomposing solid of initial particle size distribution $dG/dx = kxe^{-x^2}$

The low orders exhibited by low melting salts, in particular benzyl and methoxybenzyl derivatives, suggests that decomposition is occurring at least partially in the melt. Under the conditions of our measurements, salts pyrolyzed at or above their melting points tend to give zero-order behavior. Thus one might expect lower orders to accompany higher decomposition temperatures for any one salt, and such a tendency is observed in several cases. In this regard Pincock and coworkers have pointed out that S-shaped reaction curves may be expected in those cases where accumulation of products or by-products lowers the melting point of the sample and where the liquid substrate decomposes faster than the solid.[12]

Appendix

Evaluation of Theoretical Reaction Orders.—A distribution function is chosen, and dG/dx is plotted in terms of a unitless particle diameter x. A second curve is drawn, each point on which represents the relative weight of particles of initial diameter x remaining after a small decrement, Δx_1, in the diameter of each particle. A third curve is drawn using a larger decrement, Δx_2, in the initial diameter, and in this fashion a family of curves is constructed, as in Figure 4. [*E.g.*, a decrement d in the diameter of particles of initial diameter D reduces the relative weight of such particles to $(D - d)^3/D^3$ times their original weight as given by the distribution equation.] The area under each curve, which is proportional to the total weight of material remaining after the corresponding decrement, can be conveniently measured by means of a planimeter. Finally, because eq 1 can be simplified to eq 9, Δx is a measure of time.

$$\frac{dx}{dt} = -k \quad (9)$$

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[11] For a general discussion of nucleation, *cf.* P. W. M. Jacobs and F. C. Tompkins in "The Chemistry of the Solid State," W. E. Garner, Ed., Academic Press Inc., New York, N. Y., 1955, p 184.

[12] R. E. Pincock, K. R. Wilson, and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 6890 (1967).

Registry No.—**1a**, 14182-14-0; **1b**, 14182-15-1; **1c**, 14182-16-2; **2a**, 14182-11-7; **2b**, 14182-12-8; **2c**, 14182-13-9; **3a**, 14182-18-4; **3b**, 14182-19-5; **3c**, 14182-20-8; **4a**, 14182-25-3; **4b**, 14182-26-4; **4c**, 14182-27-5; **5a**, 14182-21-9; **5b**, 14182-22-0; **5c**, 14182-23-1; **6a**, 14181-51-2; **6b**, 14181-52-3; **6c**, 14181-53-4.

Aromatic Nucleophilic Substitution. Specific Salt Effects on Rate Constants with Benzyltrimethylammonium Methoxide in Methanol

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The reaction rate constants for the reaction of benzyltrimethylammonium methoxide (BTAM) and activated aromatic halides have been determined. The reactions are second order, but the rate constants increase with increasing concentration of BTAM. This rate increase is attributed to a specific salt effect in which benzyltrimethylammonium ion associates with the nitro group of activated aryl halide. London forces are the probable cause of this association.

The effect of added salts on the reaction of activated aryl halides and nucleophiles has been previously reported.[2] The rate constants for the reaction of 2,4-dinitrochlorobenzene with $LiOCH_3$, $NaOCH_3$, and $KOCH_3$ were found to change with changing concentrations of $M^+OCH_3^-$. The rate constant increased with increasing concentration of $KOCH_3$, but decreased with increasing concentration of $NaOCH_3$ or $LiOCH_3$ in the solvents methanol and 50% v/v benzene–methanol. For LiOH, NaOH, and KOH (in dioxane–water solvent) the rate constants decreased with increasing concentration. However, with tetrabutylammonium hydroxide as a nucleophile, the rate constants increased with increasing concentration of the nucleophile.

The decreases in rate constants can be readily understood on the basis of ion pairing, in which the ion pair ($M^+OCH_3^-$) is less reactive than the free methoxide ion.[2a] The increases in rate constant were less readily explained, for it seems unlikely that the ion pair should be more nucleophilic than free methoxide ion. The increases were tentatively attributed to a special salt effect, the association of the K^+ ion with the nitro group. It was argued that this rate-increasing effect opposed the rate-decreasing (ion-pairing) effect to give the net rate increase that was observed. The much larger rate increases observed with the tetrabutylammonium hydroxide reagent seem to involve a special salt effect. Experiments with a related nucleophile, benzyltrimethylammonium methoxide, should shed additional light on such special salt effects.

Results

The rate constants for the reaction of benzyltrimethylammonium methoxide and five activated aryl halides were determined graphically and then checked by a least-squares computer program. The least-squares constants are those reported. For 2,4-dinitrochlorobenzene, the reaction was found to be first order in the nucleophile and first order in the aryl halide. The other reactions followed second-order kinetic plots and their order was not investigated further. Products were isolated from the reaction mixtures; their purity and identity showed that the reactions are uncomplicated replacements of the aryl halide. (Details are given in Experimental Section.) In Table I the reaction rate constants for benzyltrimethylammonium methoxide are compared with those of $NaOCH_3$ as a nucleophile.

TABLE I

COMPARISON OF RATE CONSTANTS FOR THE REACTION OF SODIUM METHOXIDE AND BENZYLTRIMETHYLAMMONIUM METHOXIDE WITH THE SAME ARYL HALIDE[a]

	$NaOCH_3$		Benzyltrimethylammonium methoxide	
Substance	Temp, °C	k_2, l./mol sec	Temp, °C	k_2, l./mol sec
2,4-Dinitrochlorobenzene[b]	24.90	2.68×10^{-2}	26.70	3.30×10^{-2}
2,4-Dinitrobromobenzene[c]	25.0	1.95×10^{-2}	26.70	2.21×10^{-2}
2,4-Dinitroiodobenzene[c]	25.0	5.76×10^{-3}	26.70	7.07×10^{-3}
2,6-Dinitrochlorobenzene[d]	26.35	9.06×10^{-4}	26.70	9.06×10^{-4}
4-Cl-3,5-Dinitrobenzamide[e]	0	1.19×10^{-2}	0.06	1.24×10^{-2}

[a] Concentrations of $NaOCH_3$ are not known in every case. The change k_2 with changing concentration of $NaOCH_3$ is small for 2,4-dinitrochlorobenzene.[2] [b] Reference 2. [c] A. L. Beckwith, J. Miller, and G. D. Leahy, *J. Chem. Soc.*, 3552 (1952). [d] J. Miller, *ibid.*, 1475 (1953). [e] J. Miller, *J. Amer. Chem. Soc.*, **77**, 180 (1955).

There is general agreement between the rate constants with $M^+OCH_3^-$ and $R_4N^+OCH_3^-$.

From Figure 1, the salt effect is an increase in the rate constant for every aryl halide. The nature of the halogen displaced seems to have a slight effect on the rate constant. The per cent change in rate constant as the concentration of benzyltrimethyl ammonium methoxide concentration is changed from 0.01 to 0.08 *M* is given in Table II. For the methoxy dechlorination the per cent change is slightly greater than that for the displacement of bromine or iodine. This occurs for both methoxide and hydroxide as a nucleophile. However, the similarity in rate constant change for all substrates is more striking than these slight

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(1) Support of this research by Grant GP-4603 from the National Science Foundation is gratefully acknowledged.

(2) (a) J. D. Reinheimer, J. T. Gerig, and J. C. Cochran, *J. Amer. Chem. Soc.*, **83**, 2873 (1961); (b) J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran, and E. W. Barr, Jr., *ibid.*, **81**, 164 (1959); (c) J. D. Reinheimer and W. Hostetler, *Ohio J. Sci.*, **64**, 275 (1964).