lization from ethanol–ether gave 8.0 g (9%) of bright yellow salt, **sodium 1,2,3-tricyano-1,3-dicarbethoxypropenide (II)**, mp 241–246° dec. An analytic sample was prepared by recrystallization from ethanol, mp 299–300° dec.

Anal. Calcd for $C_{12}H_{10}NaN_3O_4$: C, 50.89; H, 3.56; N, 14.84. Found: C, 50.71; H, 3.80; N, 14.51.

The water-insoluble oil crystallized on standing 1 week. The solid was washed with ether and dried: yield 5.0 g (6%) of crude, colorless **diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa–c)**, mp 109–111°. Recrystallization from ethanol gave 4.1 g (5%) of pure IIIa–c, mp 118–119°. A mixture melting point with I was depressed, 100–104°.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.15; H, 4.48; N, 15.78.

Reaction of Triethyl *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (I) with Potassium Acetate.—Powdered anhydrous potassium acetate (3.0 g, 0.03 mol) was added to a solution of triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate in 300 ml of anhydrous glyme at 23°. The mixture was stirred for 2 days at room temperature and then evaporated to dryness under reduced pressure. The residue was recrystallized from 95% ethanol to give 4.6 g (51%) of yellow potassium 1,2,3-tricyano-1,3-dicarbethoxypropenide, mp 244–246° dec.

Anal. Calcd for $C_{12}H_{10}KN_3O_4$: C, 48.15; H, 3.37; K, 13.06; N, 14.04. Found: C, 47.96; H, 3.65; K, 13.30; N, 13.90.

The infrared absorption spectrum revealed bands at 4.54 (s) and 4.49 (w) attributable to conjugated nitrile, 5.87 (C=O), and 6.78 μ (C=C). The ultraviolet spectrum showed absorption at $\lambda_{max}^{C_2H_5OH}$ 425 mμ (ε 22,806) and 218 (13,678).

Reaction of Triethyl *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate (I) with Ethyl Sodiocyanoacetate.—A suspension of ethyl sodiocyanoacetate (0.03 mol) in anhydrous glyme was prepared by adding 3.4 g (0.03 mol) of ethyl cyanoacetate to a mixture of 1.4 g (0.03 mol) of sodium hydride (as a 50% dispersion in mineral oil) in 200 ml of anhydrous glyme at 10°. The mixture was stirred and warmed at 30° until the theoretical amount of hydrogen gas had evolved. Triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (I, 10.0 g, 0.03 mol) in 150 ml of anhydrous glyme was added at 5–10° during 40 min. After stirring overnight at room temperature, the solvent was evaporated under reduced pressure, and the red oil (approximately 30 ml) was shaken with three 100-ml portions of ether and the combined ether washings were saved. The precipitated solid, from treatment with ether, was dissolved in warm water and filtered (in several experiments some unreacted I was recovered at this point) and the filtrate evaporated to dryness. Recrystallization of the residue from ethanol gave sodium 1,2,3-tricyano-1,3-dicarbethoxypropenide (II): yield 6.6 g (78%), mp 295° dec. A mixture melting point and comparison of infrared spectra with authentic II showed them to be identical.

The ether washings were evaporated to give a mixture of orange oil and solid. The solid was collected by filtration, washed with cold ethanol and ether, and dried: yield 1.1-g (11%) recovery of starting cyclopropane I, mp 120–122°; mixture melting point with authentic I, 120.5–122°. (I was recovered in yields up to 14% in one experiment.)

The red oily filtrate was washed with water and then allowed to stand at room temperature for 1 week. During this time a white solid crystallized. The product solid was separated from the mineral oil by filtration, washed with cold ethanol and ether, and dried: yield 0.6 g (8%) of **diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa–c)**, mp 114–116°. Recrystallization from ethanol raised the melting point to 117–119°. Mixture melting point with starting cyclopropane I was depressed, 99.5–104°. Mixture melting point with authentic IIIa–c was not depressed, 118–119°. An infrared spectrum was identical with that of authentic IIIa–c. In three experiments yields of IIIa–c ranged from 4 to 8%.

Reaction of Sodium 1,2,3-Tricyano-1,3-dicarbethoxypropenide (II) with *p*-Toluenesulfonic Acid.—A solution of 2.68 g (0.014 mol) of *p*-toluenesulfonic acid in 150 ml of absolute ethanol was added to 4.0 g (0.014 mol) of sodium 1,2,3-tricyano-1,3-dicarbethoxypropenide (II) in 100 ml of absolute ethanol all at one time, with swirling, and the mixture was allowed to stand for 2 days. The red mixture was concentrated to a total volume of about 15 ml and filtered. The white solid which had been collected by filtration was washed with a small portion of cold ethanol and dried, yield 2.4 g. The solid product was then washed thoroughly with water to remove sodium *p*-toluenesulfonate and dried: yield 0.40 g (11%) of *cis*-1,2,3-tricyano-1,3-dicarbethoxypropene (VI). Recrystallization from ethanol gave 0.30 g (8.2%) of white product, mp 149.5–151°.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09; mol wt, 261. Found: C, 55.05; H, 4.24; N, 15.98; mol wt (cryoscopic method in DMSO), 245.

An infrared spectrum had absorption bands at 3.20 (C–H), 4.48 (CN), 5.95 (C=O), and 6.05 μ (C=C). The nmr spectrum showed two overlapping quadruplets (δ 4.63 and 4.60 ppm, four protons) and two overlapping triplets (δ 1.53 and 1.49 ppm, six protons), in addition to acidic proton (δ 14.65 ppm).

The filtrate from the original reaction mixture was evaporated to dryness to give an orange tacky residue. Various attempts at isolating other reaction products were unsuccessful.

Registry No.—I, 16408-63-2; II, 12259-90-4; IIIa, 16408-64-3; IIIb, 16408-65-4; IIIc, 16408-66-5; VI, 16408-67-6; potassium 1,2,3-tricyano-1,3-dicarbethoxypropenide, 12259-91-5.

Acknowledgment.—The author is deeply indebted to Dr. M. T. Jones of the Central Research Department for obtaining and interpreting the esr spectra.

Kinetics of Neutral and Alkaline Hydrolyses of Trimethylsulfonium and Benzylmethylphenylsulfonium Salts[1,2]

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Neutral Hydrolyses.—The decomposition of neutral trimethylsulfonium halides in aqueous acetone[3] or absolute ethanol[4] is a second-order process involving nucleophilic displacement of dimethyl sulfide by the anion. In contrast, trimethylsulfonium salts incorporating such relatively inert anions as perchlorate, picrate, and arenesulfonate have now been found to decompose in water solution by a first-order process. Seven different salts liberate acid at the same rate at 158°, with no important change in rate accompanying a tenfold increase in anion concentration (Table I).

Table I

Hydrolysis of $(CH_3)_3SX$

X	Concn, *M* at 25°	Addend	Concn, *M* at 25°	Temp, °C	10^5k_w, sec^{-1}
ClO_4	0.0100	None		157.8	0.37
ClO_4	0.0100	$NaClO_4$	0.100	157.8	0.37
ClO_4	0.0100	$HClO_4$	0.0100	157.8	0.39
$O_3SC_6H_5$	0.0100	None		157.8	0.41
$O_3SC_6H_4$-*p*-CH_3	0.0100	None		157.8	0.38
$O_3SC_6H_4$-*p*-Br	0.0100	None		157.8	0.36
$O_3SC_6H_4$-*p*-NO_2	0.0100	None		157.8	0.37
O_3S-β-$C_{10}H_9$	0.0100	None		157.8	0.37
OC_6H_2-2,4,6-$(NO_2)_3$	0.0100	None		157.8	0.37
ClO_4	0.0100	None		138.0	0.055

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[1] Supported in part by the National Science Foundation and by the National Institutes of Health.

[2] For further details on benzylmethylphenylsulfonium salts, see the Ph.D. Thesis of B. J. Schowen, Massachusetts Institute of Technology, Cambridge, Mass., 1964.

[3] C. G. Swain and L. E. Kaiser, *J. Amer. Chem. Soc.*, **80**, 4089 (1958).

[4] E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. Ind.* (London), 1282 (1959).

The decomposition of trimethylsulfonium perchlorate or fluoroborate in 100% ethanol at 100° is likewise independent of anion concentration.[4] The simplest mechanism consistent with these results involves a nucleophilic attack on carbon by a solvent molecule, displacing dimethyl sulfide.

Ethanolysis is more rapid than hydrolysis. The rate constant for solvolysis of trimethylsulfonium perchlorate in absolute ethanol solution at 100° is 17.8×10^{-8} sec^{-1},[3] compared to a hydrolysis constant k_w of 0.81×10^{-8} sec^{-1} extrapolated to 100° by the Arrhenius equation. This 20-fold increase in rate of solvolysis contrasts with the 20,000-fold increase in rate of decomposition of trimethylsulfonium hydroxide on changing from water to ethanol.[5]

Hydrolytic rate constants for three benzylmethylphenylsulfonium tosylates are included in Table II.

TABLE II

NEUTRAL AND ALKALINE HYDROLYSES OF BENZYLMETHYLPHENYLSULFONIUM TOSYLATES AT 60°

Benzylic substituent	$10^4 k_{H_2O}$, sec^{-1}	$10^4 k_{OH}$, M^{-1} sec^{-1}	$r^{\pm}$, Å
p-CH_3	2.00 ± 0.02	38.8 ± 3.0	1.1
H	0.2169 ± 0.0002	21.9 ± 0.2	0.9
m-Cl	0.140 ± 0.001	176 ± 3	0.7

TABLE III

DECOMPOSITION OF $(CH_3)_3SOH$

$(CH_3)_3SOH$ concn, M at 25°	Addend	Concn, M at 25°	Temp, °C	k_2, M^{-1} sec^{-1} [a]
0.0104	None		158.0	0.0117
0.00858	$NaClO_4$	0.100	158.0	0.0077
0.00846	$NaClO_4$ $NaOH$	0.082 0.0175	158.0	0.0078
0.00840	$NaClO_4$ $(CH_3)_3SClO_4$	0.082 0.0174	158.0	0.0070
0.00957	None		138.0	0.0014

[a] Second-order rate constants are corrected by 9 and 7% for the thermal expansion of water at 158 and 138°, respectively.

Alkaline Hydrolyses.—The decomposition of trimethylsulfonium hydroxide, also studied at 158°, exhibits second-order kinetics and the strong negative salt effect typical of a reaction proceeding with charge destruction (Table III). An approximate value for k_2^0, the second-order rate constant at zero ionic strength, may be calculated by means of the limiting Brønsted–Debye equation

$$\log k_2 = \log k_2^0 - 2A\sqrt{\mu}$$

by substituting for k_2 the value for the run without added inert salt and for μ the average ionic strength, 0.0060, throughout the measured course of the reaction.[6] The derived k_2^0 of 0.015 M^{-1} sec^{-1} may be compared with the second-order hydrolysis constant ($k_{w2} = k_w/50.5$) of 0.73×10^{-7} M^{-1} sec^{-1} at 158°. The drastic, but still useful, assumption that hydroxide ion and water differ in nucleophilicity only because the ion is charged[7] leads to the relation

$$\Delta F^{\ddagger}_{el} = \Delta\Delta F^{\ddagger} = -RT \ln \frac{k_2^0}{k_{w2}} = -10.5 \text{ kcal}$$

where $\Delta F^{\ddagger}_{el}$ is the electronic free energy of activation for the hydroxide reaction. From the coulomb law expression[8]

$$\Delta F^{\ddagger}_{el} = -\frac{e^2}{Dr^{\ddagger}}$$

the value of 0.7 Å is derived for $r^{\ddagger}$, the transition-state charge separation,[9] if the dielectric constant of the bulk solvent at the reaction temperature is used.

Effect of Substituents on Transition-State Charge Separation.—The neutral and alkaline hydrolyses of benzyl-, p-methylbenzyl-, and m-chlorobenzylmethylphenylsulfonium tosylates at 60° proceed with nearly exclusive cleavage of the benzyl–sulfur bond. The transition-state charge separation, $r^{\ddagger}$, calculated the same way as above (except with $[H_2O] = 54.6$ M and $D = 63$ for 60°) and tabulated in Table II, decreases when electron-withdrawing substituents are present in the benzyl portion that is undergoing displacement. This is in qualitative accord with both the reacting bond rule[10] and the more generally applicable perturbation method of Thornton,[11] which predict that, in the transition states for these reactions, electron withdrawal at the benzyl group should result in contraction of the reacting O–C and C–S bonds, and thereby reduce the charge separation.

Experimental Section

Trimethylsulfonium Salts (Table IV).—Trimethylsulfonium perchlorate, p-bromobenzenesulfonate, and p-nitrobenzenesulfonate were prepared from trimethylsulfonium iodide and the silver salt of the appropriate acid. The benzenesulfonate, p-toluenesulfonate, β-naphthalenesulfonate, and picrate were prepared by adding a stoichiometric volume of the acid to an aqueous solution of trimethylsulfonium hydroxide prepared from trimethylsulfonium iodide and silver oxide. In each case the water solution of the sulfonium salt was filtered and lyophilized. The dried salt was recrystallized using methanol for the perchlorate, ethanol for the picrate, and isopropyl alcohol for arenesulfonates.

Benzylmethylphenylsulfonium Tosylates (Table IV).—Substituted benzyl tosylates were prepared from the alcohol and p-toluenesulfonyl chloride by the general procedure of Gilman and Beaber.[2,12] Freshly prepared benzyl tosylate was dissolved in a twofold excess of thioanisole and allowed to stand for 18 hr at room temperature. The crystalline material was removed by filtration and washed with ether. m-Chlorobenzyl tosylate was treated for 3 weeks with thioanisole and enough acetone to effect solution, and the product was washed with acetone and ether. Yields were 75–85%.

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(5) J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1955).

(6) $A = 0.67$ at 158° and 0.63 at 138°. The dielectric constant of water, interpolated from the data of G. C. Akerlof and H. I. Oshry [*J. Amer. Chem. Soc.*, **72**, 2844 (1950)] is 42.3 at 158° and 46.4 at 138°. For discussion of the limiting Brønsted–Debye equation, *cf.* S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 427–430.

(7) It is also assumed that the gross mechanistic features are the same for both reactions, and that the decomposition of trimethylsulfonium hydroxide does not proceed *via* the ylide intermediate.

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 144.

(9) The electronic entropy of activation may be calculated from the relation

$$\Delta S^{\ddagger}_{el} = -(\partial \Delta F^{\ddagger}_{el}/\partial T)_p = \Delta F^{\ddagger}_{el} (\partial \ln D/\partial T)_p = 49 \text{ eu}$$

Cf. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 80–87. Activation parameters were not obtained with accuracy sufficient to provide a test of these equations, but the measured value of $\Delta\Delta S^{\ddagger}$, 35 ± 10 eu, indicates that the major difference in the rates of the two reactions is indeed an entropy effect.

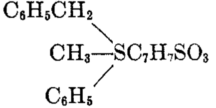
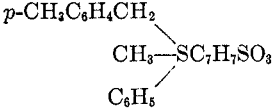
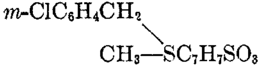
(10) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 817 (1962).

(11) E. R. Thornton, *ibid.*, **89**, 2915 (1967).

(12) H. Gilman and N. J. Beaber, *ibid.*, **47**, 518 (1925).

TABLE IV

PROPERTIES OF TRIMETHYLSULFONIUM SALTS AND BENZYLMETHYLPHENYLSULFONIUM TOSYLATES

Formula	Registry no.	Mp, °C (cor)	Calcd, %			Found, %		
			C	H	S	C	H	S
$(CH_3)_3SClO_4$		295 dec[a]						
$(CH_3)_3SC_6H_5SO_3$		166.5–168.5[b]						
$(CH_3)_3S$-*p*-$CH_3C_6H_4SO_3$	3084-73-9	173.5–175	48.55	6.49		48.53	6.37	
$(CH_3)_3S$-*p*-$BrC_6H_4SO_3$	16317-16-1	170–172	34.51	4.18		34.62	3.94	
$(CH_3)_3S$-*p*-$NO_2C_6H_4SO_3$	16317-12-7	195–196.5	38.70	4.69		38.33	4.55	
$(CH_3)_3SC_{10}H_7SO_3$	14343-63-6	187–188.5	54.90	5.67		55.22	5.81	
$(CH_3)_3SC_6H_2N_3O_7$		198–199[c]						
 $C_6H_5CH_2$ CH_3—$SC_7H_7SO_3$ C_6H_5	16317-13-8	104.5–105.5	65.25	5.74	16.59	65.43	5.87	16.56
 *p*-$CH_3C_6H_4CH_2$ CH_3—$SC_7H_7SO_3$ C_6H_5	16317-14-9	107–108	65.97	6.04	16.01	65.43	5.95	15.72
 *m*-$ClC_6H_4CH_2$ CH_3—$SC_7H_7SO_3$ C_6K_5	16317-15-0	129–131	59.92	5.03	15.23	60.56	5.48	14.92

[a] K. Lohmann (Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., Jan 1959, p 67) reports mp 292°. [b] D. Vorlander [*Ber.*, **64B**, 1736 (1931)] reports mp 164–166°. [c] T. R. Lewis and S. Archer [*J. Amer. Chem. Soc.*, **73**, 2109 (1951)] report mp 164–166°.

Kinetics of Hydrolysis of Trimethylsulfonium Salts.—Solutions were prepared quantitatively under nitrogen atmosphere using carbonate-free water, and 7-ml samples were sealed in Pyrex ampoules. Measurements were begun after the ampoules had been in the constant temperature bath for about 30 min, and reactions were followed through two half-lives. Accurate 5-ml aliquots were titrated with 0.01 *M* sodium hydroxide to the bromthymol blue end point. Because the acid generated in the reaction was consumed by the Pyrex ampoules over long periods (up to 5% consumed after 8 days at 158°), "infinite time" points were calculated, not measured. Rate constants were evaluated by conventional first-order plots.

Kinetics of Trimethylsulfonium Hydroxide Decomposition.—Solutions containing added sodium perchlorate were prepared quantitatively under nitrogen from trimethylsulfonium perchlorate, sodium perchlorate, 0.1 *M* sodium hydroxide, and carbonate-free water. Solutions containing only sulfonium hydroxide were prepared by agitating a solution of trimethylsulfonium iodide and fresh silver oxide, filtered under nitrogen pressure, and diluted to volume. Measurements were begun after the ampoules had been in the bath for about 10 min, and the reactions were followed to 80% completion. Accurate 5-ml aliquots were treated with barium chloride and titrated with 0.01 *M* hydrochloric acid to the bromthymol blue end point. Rate constants were evaluated by conventional second-order plots.

Kinetics of Hydrolysis of Benzylmethylphenylsulfonium Tosylates.—Sufficient salt to prepare a 0.1 *M* solution (0.07 *M* in the case of the *m*-chloro derivative) was dissolved in carbonate-free water, and samples were sealed in Pyrex ampoules. Because of the limited solubility of the *p*-methyl and *m*-chloro derivatives it was necessary to maintain the solution at 60° while preparing samples. Ampoules were withdrawn periodically from the constant temperature bath, and accurate 3- or 4-ml aliquots were titrated with standard 0.1 *M* sodium hydroxide to the phenolphthalein or bromocresol green–methyl red end point. Reactions were followed through at least two half-lives. The first-order rate constants for these hydrolyses were evaluated by a computer program.[13]

Kinetics of Benzylmethylphenylsulfonium Hydroxide Decomposition.—Solutions 0.1 *M* in sulfonium salt and 0.2 *M* in sodium hydroxide in carbonate-free water were prepared under nitrogen, and samples were sealed in Pyrex ampoules. At intervals the tubes were removed from the constant temperature bath, and 3-ml aliquots were added to excess standard 0.1 *M* hydrochloric acid and back titrated with standard 0.1 *M* sodium hydroxide to the phenolphthalein end point. With the *p*-methyl and *m*-chloro derivatives the reaction was rapid enough that sealed ampoules were not used. Sufficient salt to prepare 50 ml of a solution 0.1 *M* in the methyl derivative or 0.07 *M* in the chloro derivative was dissolved in carbonate-free water at 60°. Enough aqueous sodium hydroxide to make the final solution 0.2 *M* in base was quickly added, and the entire flask was immersed in the constant temperature bath. At intervals 3-ml aliquots were withdrawn and treated as above.

All reactions were followed to at least 70% completion, and "infinite time" points were measured after at least ten half-lives. Rate constants were evaluated by means of a conventional second-order plot. Because hydrolysis of the *p*-methyl compound was a significant side reaction, a special graphic method was devised to calculate the second-order rate constant for that reaction.[2]

Products of Benzylmethylphenylsulfonium Hydroxide Decomposition.—Solutions prepared as above for the kinetic runs and allowed to stand ten half-lives at 60° were neutralized with hydrochloric acid and treated with a molarity of anisole equal to the calculated benzyl alcohol or thioanisole present. A solution for comparison, prepared by combining in aqueous sodium hydroxide the precise quantities of benzyl alcohol or *m*-chlorobenzyl alcohol and thioanisole predicted to be present in the reaction mixture, was treated in the same manner with hydrochloric acid and anisole. The dried, concentrated ether extracts of the mixtures were analyzed by glpc, using 12-ft columns of Carbowax on Chromosorb P for benzyl alcohol and silicone rubber on Chromosorb P for *m*-chlorobenzyl alcohol. The ratios of peak areas were identical with ±3% for both extracts and, after correction for relative peak sensitivity, the molar ratio of anisole/thioanisole/benzyl alcohol or *m*-chlorobenzyl alcohol was 1.0:1.0:1.0. No additional products were detected.

Reaction of Carbenes with Hexafluorobenzene

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The addition of carbenes to aromatics has been well documented.[1] However, it has been suggested that

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[13] The program used was developed by K. G. Harbison from a general onlinear least squares curve fitting Fortran subroutine, ID code OR-NLLS, by Dr. P. D. Wood, Oak Ridge National Laboratory, Tenn. All computations were performed on an IBM 7090 electronic digital computer at the MIT Computation Center.

[1] See, *e.g.*, J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.