Butanol-1-*d* (from Run S).—This preparation was conducted in much the same way as that of run W, using 15.1 g. of magnesium, 67.5 g. of ethyl bromide, 81.0 g. of the 2-octanol-2-*d* prepared earlier[2] by the reduction of octanone-2 with sodium and deuteroacetic acid, having α_D −3.41° (l 0.5), and 44.6 g. of freshly distilled butyraldehyde. After two distillations through small columns a fraction, b.p. 117°, had $d^{25}{}_4$ 0.8089 and α_D $+0.026 \pm 0.006°$ (l 4). Repeat determinations at a later date gave $\alpha^{24}{}_D$ $+0.032 \pm 0.004°$, $\alpha^{24}{}_{5461}$ $+0.041 \pm 0.005°$. On refractionation, a center cut had $\alpha^{25}{}_D$ $+0.025 \pm 0.005°$, $\alpha^{25}{}_{5461}$ $+0.038 \pm 0.004°$. The yield was 18.1 g. (39%).

The density corresponds to 26 atom per cent. deuterium while the several infrared spectra taken at various times gave the values 26, 28 and 29%.

Formolysis of Butyl-1-*d* *p*-Bromobenzenesulfonate at 99°.—Butyl-1-*d* brosylate was prepared from 4.33 cc. of butanol-1-*d* from run S in the usual way. The 13.9 g. (88%) obtained in this way was maintained at 0.3 mm. for several hours at room temperature and for several minutes on the steam-bath to remove any traces of residual hexane or unreacted butanol. It then was dissolved in 200 cc. of preheated anhydrous formic acid and maintained at 99.0 ± 0.1° for 4.3 hours (4.0 half-lives). After cooling in ice and diluting with an equal volume of water, the mixture was extracted with pentane. The washed and dried pentane extracts were distilled, yielding 2.1 cc. of butyl-1-*d* formate, b.p. 104–106° and $n^{28}{}_D$ 1.3859, having $\alpha^{25}{}_D$ $+0.109 \pm 0.007°$, $+0.109 \pm 0.008°$, $\alpha^{26}{}_{5461}$ $+0.134 \pm 0.005°$, $+0.140 \pm 0.007°$, indicating 99 ± 6% and 97 ± 4% inversion, respectively.

Optical Stability of Butyl-1-*d* Formate to Acid.—Five cubic centimeters of butyl-1-*d* formate prepared from run S butanol-1-*d* (above) and 10.6 g. of *p*-bromobenzenesulfonic acid (dried in a vacuum oven overnight) was dissolved in 223 cc. of dry formic acid and maintained at 98.7 ± 0.1° for 26.5 hours. After cooling in ice and diluting with water, the mixture was extracted with pentane. After washing and drying, distillation of the pentane extract gave 2.1 g. of recovered ester, b.p. 104–106°, having $\alpha^{25}{}_D$ $-0.106 \pm 0.005°$, $-0.114 \pm 0.008°$, $\alpha^{26}{}_{5461}$ $-0.141 \pm 0.010°$, $-0.139 \pm 0.008°$, and $n^{28}{}_D$ 1.3859.

Kinetic Measurements.—For the acetolysis rates 0.1 *M* solutions of the butyl brosylate were made up with anhydrous acetic acid. Aliquots were placed in individual flasks which were tightly stoppered and placed in a thermostat. At intervals, a flask was withdrawn and its contents titrated with a 0.1 *M* solution of potassium acetate in acetic acid to a brom phenol blue end-point (yellow). For the formolysis rates, a solution 0.1 *M* in the brosylate was made up with dried formic acid.[18] This solution in a flask containing a condenser and drying tube was placed in the thermostat, zero time being taken when temperature equilibration was reached, at which point and at intervals thereafter a sample was removed and cooled to room temperature. Five cc. was then pipetted, diluted with 50 cc. of dry acetic acid and titrated potentiometrically with potassium acetate in acetic acid. The method used is quite similar to that described by Winstein[18] with the exception that the titrations were made using as electrodes a glass electrode and a silver chloride coated platinum wire, a Beckman *p*H meter being used as the potentiometer. By this method *p*-toluenesulfonic acid monohydrate in a mixture of acetic and formic acids (10:1) titrated to a neutralization equivalent of 192.2 (calculated 190.2). When titrated in acetic acid to a brom phenol blue end-point, the equivalent weight was 192.0. The results of the four runs made are recorded in Table I, the data for one run being given in Table II.

TABLE II

FORMOLYSIS OF BUTYL BROSYLATE AT 60.0 ± 0.1°

Time, sec.	Titer	10^5 *k*, sec.$^{-1}$
0	0.015	...
11890	(.47)	0.815
21150	.763	.774
35600	1.200	.755
79950	2.334	.769
95600	2.673	.778
180000	3.938	.826
268500	4.585	.860
∞	5.100	...
	Average	0.793 ± 0.031

2,4-Dimethylhexanol-4.—A sample of the alcohol[5] which had $\alpha^{25}{}_D$ −3.71 (l 2) had $\alpha^{25}{}_{5461}$ −4.34 (l 2), hence the ratio α_{5461}/α_D is 1.168.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Anion Exchange of Triphenylmethyl Chloride in Benzene Solution[1,2,3]

BY C. GARDNER SWAIN AND MAURICE M. KREEVOY[4]

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First-, second- or third-order kinetics was observed for anion exchange of triphenylmethyl (trityl) chloride with quaternary ammonium salts at 50° in homogeneous benzene solution: first order with radiochloride or fluoride (rate independent of salt concentration); second order with radiochloride and phenol (rate proportional to phenol) or with azide ion (rate proportional to salt); and third order with azide and phenol. The first-order reactions must involve a rate-determining ionization of trityl chloride aided by only the benzene. The third-order reaction must be a concerted displacement. The kinetic order reflects whether zero, one or two solute molecules have replaced benzene in solvating transition state partial charges. A competition experiment which has been done with fluoride and radiochloride in benzene solution proves the existence of a capturable intermediate.

Organic halides generally require both nucleophilic and electrophilic solvation in the transition state in order to react. Benzene is a solvent of low, but by no means negligible, nucleophilic and electrophilic solvating power, If all solvation is done by benzene, first-order kinetics must be observed. If solutes replace benzene in neither, either or both of these kinds of solvation, the kinetic order is generally first, second or third, respectively.[5]

First-order kinetics has not been observed previously for a reaction of an organic halide in such a weakly polar solvent as benzene. In the present study first-order kinetics was observed in the exchange of triphenylmethyl (trityl) chloride with a

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[1] Abstracts of 125th A.C.S. Meeting, Kansas City, Missouri, March 23–April 1, 1954, p. 22N.

[2] For further details see M. M. Kreevoy, Ph.D. thesis, M.I.T., September, 1953.

[3] Supported in part by the program of research of the Atomic Energy Commission.

[4] Moore Fellow, 1952–1953.

[5] Lower orders are possible with polyfunctional reagents (*cf.* C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2538 (1952)); higher orders occur at high concentrations (*e.g.*, above 0.2 *M* methanol, where more than one methanol molecule may be involved in electrophilic solvation).

soluble quaternary ammonium radiochloride (QCl^{36}) or fluoride (QF). This proves that the rate-determining step does not involve the salt and that all solvation must be by the benzene.

Second-order kinetics was observed previously in the reaction of methyl[6] and benzyl[7] halides with tertiary amines in benzene when no more effective electrophilic reagent than the benzene was added.

$$C_5H_4N + CH_3Br + C_6H_6 \longrightarrow C_5N_5NCH_3{}^{\oplus}Br^{\ominus}$$

Here the electrophilic solvation is by the benzene. In the present study second-order kinetics was observed in the exchange of trityl chloride with quaternary ammonium azide. This exchange proceeds so rapidly that it cannot involve a rapid ionization assisted by only the benzene, followed by a slower second step with azide. The exchange with radiochloride catalyzed by phenol is also second order (zero order in salt, first order in phenol). Here the nucleophilic solvation is by the benzene.

Third-order kinetics is very common in benzene. The methanolysis or phenolysis of triphenylmethyl (trityl) halides[8]

$$ROH + (C_6H_5)_3CCl + HOR \xrightarrow{C_5H_5N} ROC(C_6H_5)_3$$

the mutarotation of tetramethylglucose by pyridine and phenol[9]

$$C_5H_5N + \alpha\text{-D-glucose} + HOC_6H_5 \longrightarrow \beta\text{-D-glucose}$$

and the aminolysis (by pyrrole) of trianisylmethyl chloride[10]

$$C_4H_5NH + (CH_3OC_6H_4)_3CCl + C_4H_4NH \longrightarrow \alpha\text{-trianisylmethylpyrrole}$$

are all third order at low concentrations, because here the solutes are more effective than the benzene in both nucleophilic and electrophilic solvation. In the present study third-order kinetics was observed in the exchange of trityl chloride with azide catalyzed by phenol. This exchange proceeds too rapidly to involve a rapid ionization assisted by only benzene and phenol, followed by a slower second step with azide. Hence it must involve a concerted reaction of azide, trityl chloride and phenol, *i.e.*, a third-order rate-determining step.[11]

$$Q^{\oplus}N_3{}^{\ominus} + (C_6H_5)_3CCl + HOC_6H_5 \longrightarrow (C_6H_5)_3CN_3 \text{ or intermediate}$$

Exchange with Chloride.—A previous study of the exchange of trityl bromide with chloride[18] was

$$(C_6H_5)_3CBr + C_6H_5N(C_2H_5)_2{\cdot}HCl \longrightarrow (C_6H_5)_3CCl + C_5H_5N(C_2H_5)_2{\cdot}HBr$$

complicated by rates too fast for convenient measurement and determination of kinetic order, and by the presence of acids (tertiary ammonium chloride and hydrogen chloride in dissociation equilibrium with it) and a base (tertiary amine from the dissociation equilibrium). In the present study we used trityl chloride to give a slower rate, and quaternary dimethyldioctadecylammonium salts (QY) as anion donors at 50° in benzene solution to avoid the presence of acids and bases. Benzene is an ideal inert solvent for kinetic studies because it

$$(C_6H_5)_3CCl + QY \longrightarrow (C_6H_5)_3CY + QCl$$

easily can be prepared pure and dry, it cannot tautomerize or eliminate water by condensation (as acetone does), and it is unlikely to mask completely the nucleophilicity or electrophilicity of added solutes through a high reactivity of its own. The quaternary salts could not be purified completely, but the results indicate that the impurities did not affect significantly the rates (see section on impurities). Hereafter these quaternary salts will be designated merely by the names of their anions.

The exchange of trityl chloride with radioactive chloride ($Y = Cl^{36}$) in benzene solution was first order in trityl chloride and zero order in salt from 0.0006 to 0.007 M salt. Table I gives typical kinetic data.[2] The rate of any homogeneous isotopic exchange reaction in which no chemical change takes place, in which the exchanging atom has only

TABLE I

RADIOCHLORIDE EXCHANGE OF 0.032 M TRITYL CHLORIDE AT 50° IN BENZENE SOLUTION[a]

Run	QCl^{36}, M	Addend, M	$R(a + b)/ab$,[b] min.$^{-1}$ × 10^2	R/a, min.$^{-1}$ × 10^3	$t_{1/2}$, min. Obsd.	$t_{1/2}$, min. Calcd.[c]
21	0.0011	....	13.8 ± 1.1	4.5	5.0	4.8
19	.0033	....	4.87 ± 0.31	4.6	14.2	13.8
14	.0066	....	2.77 ± .15	4.7	25.0	25.1
17	.0132	....	3.64 ± .24	10.6	19.2	43
27[d]	.0328	....	35.5 ± 3.0	181	2.0	75
26	.0011	0.017 QF	2.37 ± 0.22	0.8	29.2	5.1
28[d]	.0064	.002 C_6H_5OH	9.6 ± 1.2	16	7.2	6.9
30[e]	.0064	.011 C_6H_5OH	56 ± 4	96	1.2	1.6

[a] Sample runs only[2]; fifteen runs were done at 50°. Run numbers are chronological. [b] Calculated from equation 1; second figure given is average deviation from mean for all kinetic points of the run. [c] Half-life calculated from equation 3, neglecting second term of equation 2. Run 26 calculated assuming fluoride has no effect. [d] 0.031 M trityl chloride. [e] 0.030 M trityl chloride.

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(6) C. G. Swain and R. W. Eddy, THIS JOURNAL, **70**, 2989 (1948).

(7) C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).

(8) C. G. Swain, *ibid.*, **70**, 1119 (1948).

(9) C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2534 (1952).

(10) L. E. Kaiser, Ph.D. thesis, M.I.T., January, 1954.

(11) In this paper we avoid using the words "termolecular" or "molecularity" because they have been defined ambiguously. Originally "molecularity" was thought to be synonymous with over-all kinetic order.[12] It is now recognized as a theoretical rather than an empirical concept.[13] Ingold[14] defined molecularity as "the number of molecules necessarily undergoing covalency change" in the rate-determining step of a reaction. This still requires the user to make a subjective choice of which molecules to include, because all chemical interactions have some covalent character.[15] Ingold chooses to interpret it so narrowly as to exclude hydroxylic species and Lewis acids which seem to be bonded to a halide in the transition state.[16] Hammett, on the other hand, used the term to designate the total number of molecules which participate significantly in the rate-determining step.[17] By this criterion many reactions in solution are probably highly polymolecular. However, to be completely unambiguous, it seems wise at present to avoid the term "molecularity" and to discuss instead the "kinetic order of the rate-determining step." The "rate-determining step" is defined as the step which has the smallest rate along what is nevertheless the fastest route from reactants to products. For many reactions the rate-determining step is still not known with certainty, but every reaction must have one, and it becomes known with more certainty as information accumulates on the existence and concentrations of intermediates.

(12) S. Arrhenius, *Z. physik. Chem.*, **1**, 110 (1887).

(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 11.

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 315.

(15) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, Chapter 2.

(16) C. K. Ingold, ref. 14, p. 357.

(17) N. T. Farinacci and L. P. Hammett, THIS JOURNAL, **59**, 2542 (1937).

(18) C. G. Swain, *ibid.*, **72**, 2794 (1950).

two forms, and in which the isotope effect can be neglected is[19]

$$R = (2.303 \log (1 - z)/t)\,(ab)/(a + b) \qquad (1)$$

where z is the fraction of complete exchange at time t, and a and b are the total (radioactive plus inert) concentrations of the two chemical species between which the element is being exchanged (here $(C_6H_5)_3CCl$ and QCl), which are constant within any given run. Plots of log $(1 - z)$ *vs.* t appeared free from curvature, confirming that no chemical change was taking place. The average deviation in R values calculated from all kinetic points in a given run ranged from 4.1 to 12.5% for 15 different runs at 50°, and averaged 6.6%.

At higher concentrations of chloride ion than 0.007 *M*, the rate depended on the concentration of salt.

$$R = k_1a + k_3ab^m \qquad (2)$$

Values of k_1, k_3 and m are given in Table II. The higher-order second term of equation 2 was not investigated except to determine the maximum salt concentration at which it could be neglected, but it is thought that it probably represents a second-order rate-determining step between trityl chloride and larger-than-average aggregates rather than a true polymolecular reaction. Below 0.007 *M* salt, the second term may be neglected because it contributes less than 12% to the total rate.

Table II

Rate Constants for Anion Exchange of Trityl Chloride in Benzene Solution

Salt	Catalyst	Temp., °C.	Rate constant	Value[a] and mean deviation	No. of runs
QCl^{36}	None	50.0	k_1	$7.9 \pm 0.4 \times 10^{-5}$ sec.$^{-1}$	7
QCl^{36}	None	36.0	k_1	$3.3 \pm 0.1 \times 10^{-5}$ sec.$^{-1}$	2
QCl^{36}	None	67.7	k_1	23.4×10^{-5} sec.$^{-1}$	1
QCl^{36}	QCl	50.0	k_3^b	$99 \times 10^2\ M^{-3.7}$ sec.$^{-1}$ ($m = 3.7$)	1
QCl^{36}	C_6H_5OH	50.0	k_2^c	$10.5 \pm 1.2 \times 10^{-2}\ M^{-1}$ sec.$^{-1}$	4
QF	None	50.0	k_1^d	$9.5 \pm 0.7 \times 10^{-5}$ sec.$^{-1}$	11
QN_3	None	50.0	k_2^e	$3.3^f \times 10^{-2}\ M^{-1}$ sec.$^{-1}$	2
QN_3	C_6H_5OH	50.0	k_3^g	$1.6 \pm 0.2 \times 10^1\ M^{-2}$ sec.$^{-1}$	3

[a] Correctly based on natural logarithms. [b] From equation 2. [c] For phenol-catalyzed term from equation 3. [d] From initial rates. [e] For uncatalyzed reaction. [f] Value for 0.03 *M* salt. Higher values observed at lower and higher concentrations are 4.5×10^{-2} for 0.014 *M* salt, 3.6×10^{-2} for 0.054 *M* salt. [g] For phenol-catalyzed term based on $k_2 = 3.3 \times 10^{-2}$ and calculated using excess azide over the phenol (free or uncomplexed azide), but stoichiometric concentration of phenol (0.004–0.008 *M*). If free phenol were known and were used in the calculations, this coefficient would probably be larger by a factor of two to ten.

Phenol catalyzed the reaction strongly; as little as 0.002 *M* phenol increased the rate more than threefold. Thus electrophilic solvation is extremely important in this reaction and trityl chloride discriminates much more highly among different electrophilic reagents in this halide exchange reaction than methyl bromide does in the Menschutkin reaction.[6] Below 0.007 *M* salt, the increment in rate was proportional to the phenol concentration and independent of the salt concentration (b).

$$R = k_1a + k_2a(C_6H_5OH) \qquad (3)$$

The catalytic coefficient of phenol is the same, within experimental error, with concentrations of phenol both lower and higher than the chloride concentration.

The reversible ionization of trityl chloride has been demonstrated previously in *m*-cresol,[20] in nitroalkanes[21] and liquid sulfur dioxide.[22] In addition the trityl cation has been demonstrated as an intermediate in the solvolysis of trityl chloride in aqueous acetone.[23]

Temperatures of 36, 50 and 67.6° were used to study the uncatalyzed exchange with chloride ion. A plot of log (k_1/T) *vs.* $1/T$ was a straight line. The calculated heat (ΔH^*) and entropy of activation (ΔS^*) were 12.4 ± 0.7 kcal. mole^{-1}, and −39 cal. deg.$^{-1}$ mole^{-1} at 50°. This heat of activation is close to the value (12.0 kcal.) obtained for the ionization of trityl chloride in 85% acetone–15% water at low temperatures.[24] A large negative entropy of activation, such as was found here, is to be expected for an ionization in a medium of low dielectric constant.[25]

Fluoride (0.017 *M* QF) produced a sixfold diminution in the rate of exchange with 0.0011 *M* chloride ion. The concentrations in this run were so chosen that less than 10% of the trityl chloride was actually consumed by the fluoride during the time over which the exchange with radiochloride was followed. When coupled with evidence given in the next section that the total rate is unchanged, this indicates the presence of a capturable intermediate.

The mechanism proposed to account for these results is

$$\text{TCl (or TCl}^*) \underset{k_r}{\overset{k_1}{\rightleftarrows}} \text{T}^{\oplus}\text{Cl}^{*\ominus}$$

$$\text{T}^{\oplus}\text{Cl}^{\ominus} + \text{Q}^{\oplus}\text{Cl}^{*\ominus} \underset{k_x}{\overset{k_x}{\rightleftarrows}} \text{T}^{\oplus}\text{Cl}^{*\ominus} + \text{Q}^{\oplus}\text{Cl}^{\ominus}$$

$$\text{T}^{\oplus}\text{Cl}^{\ominus} \text{ (or T}^{\oplus}\text{Cl}^{*\ominus}) + \text{Q}^{\oplus}\text{F}^{\ominus} \underset{k_z}{\overset{k_y}{\rightleftarrows}} \text{T}^{\oplus}\text{F}^{\ominus} + \text{Q}^{\oplus}\text{Cl}^{\ominus}$$

$$\text{T}^{\oplus}\text{F}^{\ominus} \underset{k_0}{\overset{k_p}{\rightleftarrows}} \text{TF}$$

where the k_1 step is rate determining, and $k_z \cong k_y \cong k_x >> k_r \cong k_p >> k_1 > k_0$. Exchange (the k_x step) must be faster than reversion of the exchangeable ion pair to starting material (the k_r step) because the rate (R) is independent of salt (QCl* or QF) concentration. The ion-pair intermediates would be undissociated in this medium but solvated by benzene. Assuming a rapid, statistical distribution between them ($k_z = k_y = k_x$), one can calculate that $k_p = 5.7\,(0.0011)k_r/0.017 = 0.37k_r$.[26]

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[19] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 1.

[20] A. Hantzsch, *Ber.*, **54**, 2573 (1921).

[21] A. Bentley, A. G. Evans and J. Halpern, *Trans. Faraday Soc.*, **47**, 711 (1951); *J. Chem. Soc.*, 3468 (1952).

[22] N. N. Lichtin and P. D. Bartlett, This Journal, **73**, 5530 (1951).

[23] C. G. Swain, C. B. Scott and K. H. Lohmann, *ibid.*, **75**, 136 (1953).

[24] C. G. Swain and C. B. Scott, *ibid.*, **75**, 246 (1953).

[25] A. A. Frost and R. G. Pearson, ref. 13, p. 127.

[26] This is not a surprising result because fluoride is usually a little less nucleophilic than chloride. With methyl bromide at 50° in 50% acetone–50% water its nucleophilic constant is about 1.8 (J. Bloomfield) *vs.* 3.0 for chloride (C. G. Swain and C. B. Scott, This Journal, **75**, 141 (1953). With trityl fluoride at 50° in 70% acetone–30% water the rate of hydrolysis was decreased threefold by substituting 0.1 *M* potassium fluoride for 0.1 *M* potassium nitrate.[3]

Ingold[27] reclassified our methanolysis or phenolysis of trityl chloride in benzene solution[8] as an SN2 reaction, *i.e.*, a one-step reaction not involving a carbonium ion, because it was run "in the completely non-ionizing solvent, benzene." However, ionization is the rate-determination step for exchange with chloride ion with only benzene solvating the carbonium chloride ion pair. Moreover, the phenol-catalyzed rate of ionization at 25° would be much faster than the phenol-catalyzed methanolysis with the concentrations used. This precludes the argument that ionization is too difficult in benzene and suggests that the rate-determining step with hydroxylic species is either a third-order ionization process or else a reaction of a singly-solvated ion pair with the second hydroxylic molecule (*e.g.*, $(C_6H_5)_3C^{\oplus}Cl^{\ominus}\cdot HOC_6H_5 + CH_3OH$).

Exchange with Fluoride.—The exchange of trityl chloride with dimethyldioctadecylammonium fluoride in benzene solution at 50° was likewise first order in trityl chloride and zero order in salt from 0.016–0.065 *M* fluoride and the first-order rate constant ($9.5 \pm 0.7 \times 10^{-5}$ sec.$^{-1}$) was nearly within experimental error of that for exchange with radioactive chloride ($7.8 \pm 0.4 \times 10^{-5}$ sec.$^{-1}$). The difference is attributed to a salt effect since the concentration of salt is higher in these experiments than in those with radiochloride (which were 0.0006–0.007 *M* chloride). The methanolysis of trityl chloride in benzene also shows a small positive salt effect.[8]

Chloride added in concentrations comparable to the fluoride (0.02–0.05 *M* chloride) did not inhibit the exchange with fluoride. This is understandable because chloride exchange cannot change the reactivity of the trityl chloride.

All the rate constants for exchange with fluoride ion were obtained from initial rates, since this reaction follows first-order kinetics only to about 40% reaction, then slows down rapidly to less than 1% of the initial rate after it has consumed about 50% of whichever reactant is in lower concentration. The reaction is not reversible, since 0.017 *M* trityl fluoride and 0.021 *M* chloride gave less than 3% of trityl chloride after one month under the same conditions. Neither of the products stopped the reaction when they were added initially along with the reagents.

Exchange with Azide.—The exchange of trityl chloride with dimethyldioctadecylammonium azide in benzene solution at 50° was first order in trityl chloride and first order in salt, hence second order over-all within any given run. The exchange was irreversible and ran to completion. There was some variation in the value of the second-order rate constant with different initial salt concentrations, but it was neither consistent nor large enough to suggest that the order was anything but second. The reason for this constancy within runs and slight variation between runs is discussed more completely in the section below on "state of aggregation of salts in benzene solution."

We picture the uncatalyzed exchange with azide as a simple reaction between trityl chloride and a salt particle, or else a second-order rate-determining ionization involving nucleophilic solvation by azide, followed by a fast collapse of the trityl azide ion pair. One mechanism which is excluded is a prior ionization assisted by only the benzene followed by a rate-determining reaction with azide ion, since the rate of ionization assisted by only the benzene is known from the exchange with radiochloride and is much slower than the rate of exchange with azide.

Exchange with Azide Catalyzed by Phenol.—That phenol catalyzes the reaction is immediately evident from the initial rates. Since phenol is not consumed in the course of the reaction, one might expect the simple second-order rate law still to be obeyed. Examination of the constants calculated for each point within a run shows that it is not, the "constants" showing a systematic decrease of a factor of two. In order to obtain constants showing no systematic drift, it was necessary to subtract the phenol concentration from the stoichiometric azide concentration, indicating that most of the phenol is hydrogen-bonded to azide in a 1:1 complex. By considering that the complex is a phenol donor but not an important azide donor and that only the excess azide is reactive, constant second-order constants for reaction with azide were obtained. However, the exchange does continue at about one-fifth the rate it would have with no phenol present, after the excess azide has been consumed.

The phenol-catalyzed exchange with azide is pictured as a mechanism with a third-order rate-determining step leading either directly to products or to an intermediate trityl chloride ion pair (with the trityl ion solvated by azide ion and the chloride ion solvated by phenol) which rapidly collapses to trityl azide. One mechanism which is excluded is a prior ionization assisted by only the benzene and phenol, followed by a rate-determining reaction with azide ion, since the rate of ionization assisted by only benzene and phenol is known from the phenol-catalyzed exchange with radiochloride and is much slower than the phenol-catalyzed exchange with azide.

State of Aggregation of Salts in Benzene Solution.—Kraus, Fuoss and their co-workers have examined the state of aggregation of salts in benzene solution, using the methods of molecular polarization,[28] conductance,[29,30] and freezing point depression.[31] All of the salts studied showed some aggregation, at least at higher concentrations. Molecular polarizations, which are determinable at very low concentration, showed that quaternary ammonium salts other than picrates dimerize at concentrations as low as 5×10^{-5} *M*. With salts which are sufficiently soluble for measurements at concentrations up to 1 *M*, the equivalent conductances showed both maxima and minima[29] while the molecular weight determined by freezing point depression went through a maximum corresponding to an aggregation number of 20–30.[31] Some of the less soluble salts showed a very high degree of aggrega-

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[27] C. K. Ingold, ref. 14, p. 356.

[28] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 586 (1936).

[29] L. E. Strong and C. A. Kraus, THIS JOURNAL, **72**, 166 (1950).

[30] H. S. Young and C. A. Kraus, *ibid.*, **73**, 4732 (1951).

[31] D. T. Copenhafer and C. A. Kraus, *ibid.*, **73**, 4557 (1951); C. H. Keith and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **39**, 598 (1953).

tion even at very low concentrations; tri-*n*-butyloctadecylammonium formate, for example, showed an aggregation number of 21.5 at a concentration of 3.2 × 10^{-3}.[31] In all cases the degree of aggregation was a sharp function of concentration.

Of special interest are Kraus' findings with 1:1 mixtures of tetraisoamylammonium thiocyanate and tetra-*n*-butylammonium thiocyanate.[31] The apparent molecular weight of the mixture was determined by measurements of freezing point depression, and the aggregation number for the mixture was very precisely given by the mean of aggregation numbers that the pure salts would have given each at the total salt concentration. This implies a random distribution of species in the aggregates. It also indicates (a result which is very important for the present work) that if two salts have similar aggregation numbers one can be continuously substituted for the other with no great change in the state of aggregation.

In order to check the qualitative applicability of these results to the present system, the molecular weight of dimethyldioctadecylammonium azide was determined by Mr. R. L. Cleland from light scattering measurements. The average molecular weight of 0.062 *M* azide at 29° was 14,000, corresponding to an average aggregation number of about 30.

The empirical second-order rate constant for the exchange between trityl chloride and azide is $\sum_n (f_n k_n)$ where f_n is the fraction of azide (QN_3) having aggregation number n and k_n is the corresponding rate constant. The sum will be a constant within a given run if k_n/n is a constant or if n, the average aggregation number, does not change as chloride is substituted for azide in solution. If k_n/n is a constant the reactivity of azide is independent of its state of aggregation and proportional to its concentration. Although it is quite reasonable that k_n should increase with n, a linear relation seems improbable. Since dimethyldioctadecylammonium chloride and azide have the same cation and have anions of approximately the same size and charge type, it is quite likely that, independently, they have similar aggregation numbers. In that case Kraus' work with mixed salts, described above, indicates that n would remain constant as chloride was substituted for azide, giving the observed second-order rate law within any given run. Since n would be expected to change with over-all salt concentration, the observed second-order rate constant would also be expected to change from one run to another, as it did.

Possible Effects of Impurities.—The quaternary dimethyldioctadecylammonium salts used could not be purified to the point of giving satisfactory analytical data (see Experimental section). Therefore it is necessary to consider whether the presence of impurities permits any alternative interpretations instead of the conclusions above. The salts probably were contaminated with both octadecyl bromide and water.

It seems unlikely that the covalent bromide could have affected the rates. *n*-Butyl bromide in dry acetone has been shown not to exchange with lithium bromide ion pairs but only with the dissociated bromide ion,[32] hence an aliphatic primary or secondary alkyl bromide would be unlikely to react with the present salts in benzene solutions.

The following results indicate that the rates were not influenced by the presence of water. If water were a catalyst and its concentration were proportional to the concentration of the salt, the rate constants from one run to another would vary regularly with the initial salt concentration. In none of the reactions studied was this found to be the case, although the chloride concentration was varied over a factor of 60 and the azide and fluoride concentratrations over a factor of 4. The reactions with fluoride and low concentrations of chloride apparently go *via* ionization of trityl chloride, and their rates vary by less than 20%, in spite of the fact that the fluoride apparently has more than twice as much water as the chloride. The rate of the reaction with azide is dependent on azide concentration, raising the possibility that an effect of water may be masked, but one run which was done with anhydrous salt (although still not pure, see Experimental section) gave a rate constant differing less than 10% from that for the hydrated salt.

Two results remain on which water may have an effect: the catalysis of the azide reaction by phenol may be due actually to water displaced from an azide complex by the phenol; and the high-order second term of the uncatalyzed chloride exchange may be due actually to catalysis by water. The catalysis of the chloride exchange by phenol cannot be affected by water since variation of the chloride (and, thereby, the water) concentration does not affect the rate constant. The stopping of the fluoride reactions cannot be explained by consumption of the trityl chloride by the water because in runs where there is a twofold excess of trityl chloride the fluoride is still not all consumed.

Experimental

All melting points are corrected and all boiling points are uncorrected.

Long Chain Salts.—Kraus and co-workers have prepared many benzene-soluble salts, but most of them were either tertiary salts, with an undesirable acidic hydrogen, or else had an exotic anion, such as picrate or thiocyanate. For the present work a quaternary ammonium cation was desired that would solubilize a series of anions in benzene, including the simple halides. Since the Armour "Arquad 2 H T" (impure dimethyldioctadecylammonium chloride) was known to be soluble in benzene, at least at slightly elevated temperature, dimethyloctadecylammonium and di-*n*-butyldioctadecylammonium salts were examined. Both were found to be difficult to prepare and very difficult to purify. Of the two, the dimethyldioctadecylammonium salts were chosen as the more suitable in spite of the fact that they could never be purified completely, because they crystallized quite well from acetone, nitromethane, or acetonitrile even when impure. The di-*n*-butyldioctadecylammonium salts came out of solution as a gel.

***Dimethyldioctadecylammonium* Bromide.**—Octadecyl bromide (10 g. Eastman Kodak Co. white label, 0.030 mole), dimethyloctadecylamine (10 g. of Eastman Kodak Co. technical, 0.033 mole), 250 ml. of acetonitrile (Carbide and Carbon commercial solvent, redistilled, b.p. 80.2–81.0°), and 50 ml. of benzene (Mallinckrodt reagent, thiophene-free, added to bring the refluxing mixture into homogeneous solution) were refluxed for 10 days and the solution was cooled in a refrigerator overnight. The crude product, which crystallized as a tawny mass, was filtered, dissolved

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(32) C. G. Evans and S. Sugden, *J. Chem. Soc.*, 270 (1949).

TABLE III

ANALYTICAL DATA

Compound	M.p.,[a] °C.	Calcd. for anhydrous salt C	H	N	X[b]	X[c]	Calcd. for monohydrate C	H	N	X[b]	X[c]	Found C	H	N	X[b]	X[c]
Bromide	161–163	71.90	12.71	2.21	13.18	12.58	69.92	12.66	2.15	12.81	12.24	71.27	12.90	2.17	12.72	12.40
Chloride	149.4–151	77.32	13.66	2.37	6.29	...	75.03	13.58	2.30	6.10	....	76.23	13.34	..	6.48	...
Fluoride	Indefinite	79.53	14.05	2.44	...	3.31	74.86[f]	13.89[f]	2.30[f]	...	3.03[f]	73.45	13.80	..	...	2.96
Azide	Indefinite	76.47	13.51	9.40	...	9.40	74.23	13.44	9.24	...	6.93	74.09	13.54	..	...	6.17
Bromide[d]	158–159	...			...	...		....	...	...	....	70.94	12.76	2.64	12.04	...
Azide[e]	Indefinite	...			...	...		....	...	...	....	75.00	13.55	..	...	...

[a] Corrected. [b] Carius value (includes covalent Br). [c] Titrimetric value (does not include covalent Br). [d] Obtained from salts recovered from reaction mixture. [e] Dried over CaH_2. [f] Calculated for $2H_2O$.

in 300 ml. of warm benzene and allowed to stand for 24 hours over calcium hydride (Metal Hydrides, grade I) at 50°. The solution was then diluted with an equal volume of benzene and passed directly onto an 8-inch high × 1.3-inch diameter column of activated alumina (Merck reagent, "suitable for chromatographic adsorption," heated in a free flame for 2 hours, cooled in a desiccator, and washed with benzene before using). If the solution applied to the chromatographic column was too concentrated, it gelled on cooling, making it impossible to pass solvent through the column. The chromatogram was washed with 200 ml. of benzene and developed with 5 liters of 50% benzene–50% acetone (reagent grades). This removed non-polar impurities (*i.e.*, unreacted starting materials, olefin formed by elimination, amine formed from amine hydrobromide by treatment with calcium hydride, octadecyl alcohol and other non-polar materials which may have been present as impurities in the starting materials). The product, dioctadecyldimethylammonium bromide, was obtained in 25–40% yield (5–8 g.) by eluting the column with 5 liters of acetone, concentrating the solution to 100 ml., crystallizing in the refrigerator, then recrystallizing twice from acetonitrile, m.p. 161–163°.

Other Anions.—The other dioctadecyldimethylammonium salts were obtained in nearly quantitative yield from the bromide by passing a 2% solution of the latter in 95% ethanol (U.S.I. pure grade denatured with methanol) over a 25–50 fold excess of National Aluminate Co. Nalcite S.B.R. (a polystyrene quaternary ammonium salt ion-exchange resin of mesh −20 to +50 (Tyler standard)) bearing the appropriate anion. Fifty ml. of the resin, obtained as the chloride, was packed in a 100-ml. buret by back-washing with distilled water, then the chloride was exchanged for the proper anion by passing through a 1 *M* solution of reagent grade potassium fluoride or bromide or Eastman Kodak Co. practical grade sodium azide at the rate of one drop per second. The column was washed with 500 ml. of distilled water, then with 500 ml. of 95% ethanol and repacked. The solution of bromide was passed through at about one drop every two seconds, followed by about 300 ml. of alcohol. The eluate was collected and the alcohol removed under vacuum at room temperature. The product was recrystallized twice from acetonitrile or acetone.

Radiochloride was prepared from inactive chloride in much the same way except that an equimolar quantity of resin was used. Radiochloride was transferred to the resin by washing with 0.00118 *M* HCl^{36} purchased from the Atomic Energy Commission.

Identity and Purity of the Salts.—Elementary analysis of the salts revealed serious discrepancies with calculated values. The azide, when dissolved in 95% ethanol and strongly acidified with nitric acid, gave no precipitate with alcoholic silver nitrate. Nevertheless Carius analysis for Br revealed 0.64%. This was assumed to be bound covalently to one of the alkyl residues of the cation and therefore present in all the salts. Infrared spectra of the chloride, the fluoride and the azide all showed the presence of hydrogen on nitrogen or oxygen.[2] Amine impurities were excluded by the fact that the salts were neutral to crystal violet in glacial acetic acid, and ammonium salts were excluded because the salts were neutral to *m*-cresol purple in a 1:1 mixture of aniline and alcohol. Contamination by water would account for both the spectra and the analysis (after correction for the covalent bromine), but an integral number of water molecules can be assigned only to the azide. The melting points and analytical results are shown in Table III. The water could not be removed by drying in an Abderhalden pistol below the melting points.

The ultraviolet spectrum of the azide in 95% ethanol agreed very closely with that of sodium azide (assuming quaternary azide to be pure),[2] showing that the impurities must be of low molecular weight and colorless in the ultraviolet. Water again is indicated.

To determine the effect of the water on the reaction rates a sample of the azide was dissolved in warm benzene and allowed to stand over calcium hydride for 4 days. This would presumably remove any impurity having a hydrogen on oxygen or nitrogen. The solution was evaporated and the product used directly in one run after drying under vacuum. The rate constant was the same as before but only 82% of the theoretical quantity of trityl chloride was consumed, indicating the presence of unreactive impurities. The elementary analysis of this compound is shown in Table III.

Light Scattering.—The turbidity of an 0.062 *M* azide solution in benzene was determined by Mr. R. L. Cleland. We are indebted to Professor W. H. Stockmayer for making the equipment available. The solution was cleaned by filtration through ultrafine-porosity sintered-glass filters under pressure. This procedure was not entirely satisfactory in removing dust as shown by dissymmetry in the scattering about 90° with the incident beam. This could be reduced by repeated filtration without affecting the scattering at 90°, but the lowest value obtained for the dissymmetry coefficient (ratio of intensity of scattered light at 45° to that at 135°) was 1.2. In calculating the molecular weight the dissymmetry was neglected because it is always found to be negligible for particles of this size. The correction for a coefficient of 1.2 would increase the molecular weight by about 20%. The scattering observed at 90° was assumed to be true solute scattering because of its observed constancy with varying amounts of dust. The molecular weight was calculated from the turbidity in the usual way by equation 4.[33]

$$Hc = \frac{1}{M} + 2Bc \tag{4}$$

where

H = constant depending on the experiment
c = concentration of solute g. ml.$^{-1}$
τ = excess turbidity of solution over solute, cm.$^{-1}$
M = molecular weight
B = second virial coefficient depending on the solute solvent system

The usual extrapolation to zero concentration to obtain *M* was not possible in this case because the state of aggregation varies with concentration. For this reason the terms after the first one on the right-hand side of (4) were neglected in calculating *M*. The effect of this should be small because *B* should be small for a system near the precipitation temperature. A value of 14,000 was calculated for *M* in this way.

Trityl Chloride.—Trityl chloride was prepared from triphenylcarbinol and acetyl chloride[34] in 57% yield (70 g.), m.p. 111.5–113°, % titrable acid by quantitative solvolysis in 80% acetone, 100.1, 100.0%.

Trityl Fluoride.—Trityl chloride (20 g.) was treated with liquid hydrogen fluoride for 30 minutes. The hydrogen fluoride was boiled off and the product, a brown solid, was crystallized from 100 ml. of anhydrous ether (Mallinckrodt reagent grade dried over sodium wire) at Dry Ice temperature, yielding a yellow solid. This was added to 10 ml. of acetic anhydride (Merck 96.5%) and several ml. of hydro-

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[33] P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

[34] W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

gen fluoride were added. The mixture was heated to effect solution, then 80 ml. of anhydrous ether was added and the product was crystallized at Dry Ice temperature. The process was repeated with 8 ml. of acetic anhydride and 50 ml. of ether, except that before crystallization the ether solution was allowed to stand overnight over calcium hydride. All transfers up to the time the excess hydrogen fluoride was destroyed with calcium hydride were made in a dry-box. The product, trityl fluoride, was a white crystalline solid, m.p. 100.4–103.2°, free of hydrogen fluoride (neutral to phenolphthalein in 90% aqueous acetone); purity by titration with base in 50% aqueous acetone, 99.7%, 99.8%.

Other Reagents.—All benzene used in kinetic runs was Mallinckrodt reagent grade stored over sodium wire. Aniline was Mallinckrodt reagent grade freshly distilled from sodium hydroxide pellets. Standard base was prepared by decanting a saturated solution of sodium hydroxide (Mallinckrodt analytical reagent grade) in water and diluting with freshly boiled distilled water. It was standardized periodically by titrating benzoic acid (U. S. Bureau of Standards primary standard) under the conditions of the determinations being made.

Products.—The exchange with chloride leads to no chemical change. This is confirmed by adherence to the first-order exchange law.

Scott isolated trityl azide from the reaction of trityl chloride with sodium azide in acetone–water mixtures.[23] The conditions of the present exchanges with azide seem, if anything, much less likely to result in any other product.

Trityl fluoride was shown to be the product of the exchange with fluoride by determining its rate of solvolysis at 50° in a solution of 26% water, 61% acetone, 9% benzene and 4% aniline (the quenching solution). The method of intermittent titration was used.[35] The half-life, 87 minutes, was in acceptable agreement with the half-life of 60 minutes obtained at 50° in 70% acetone–30% water with an authentic sample.

Quaternary ammonium salt was reisolated from the fluoride exchange reaction mixture as follows. After titration all the aliquots from two runs were collected, the organic solvents boiled off, and the solid residue filtered. This was crystallized four times from acetone to remove trityl compounds, the product was dissolved in 95% ethanol and converted to the bromide on the ion exchange resin as described. The bromide (m.p. 158–159°) was obtained in 75% yield (2.4 g.), and its elementary analysis is shown in Table III.

Kinetic Methods for Azide and Fluoride.—Both reactants were weighed out, dissolved in benzene, and brought to 50° before mixing. When phenol was used it was first pipetted from a standard solution (in dry benzene) into the azide solution.

On quenching the azide reactions in aqueous acetone or alcohol, a large fraction (about 60%) of the reaction took place after quenching. Aniline, a very good nucleophilic reagent, therefore was used as a quenching medium. To 10-ml. portions of aniline, 5-ml. aliquots of the reaction mixture were added, then 10 ml. of 95% ethanol. The hydrogen ion, which was liberated quantitatively by the trityl chloride under these conditions, was titrated with standard base. Trityl azide was unaffected.

Runs with fluoride were prepared and started in the same way as runs with azide. Each was quenched in a mixture of 50 ml. of acetone, 15 ml. of water and 2 ml. of aniline. The aniline was necessary to eliminate capture of trityl ion by fluoride ion in the quenching medium. Hydrogen ion liberated by the trityl chloride was titrated again with base. Trityl fluoride under these conditions has a half-life of about one day at 25°.

Radioactive Chloride.—Runs were prepared and started as above. In order to separate the trityl chloride from the quaternary ammonium salt, aliquots of the reaction mixture were passed over anhydrous ion exchange resin (Nalcite S.B.R., acetate form), which adsorbed the salt quantitatively but passed the trityl chloride unchanged. Ten ml. of the resin was first packed in a 50-ml. buret, converted to the acetate form with 250 ml. of 1 *M* reagent potassium acetate, washed with 250 ml. of 95% ethanol to remove any potassium acetate and lower the water content, then washed with 220 ml. of benzene. A column prepared in this way adsorbed 0.03 mole of dioctadecyldimethylammonium chloride from 60 ml. of anhydrous benzene (no precipitate with alcoholic silver nitrate).

Five-ml. aliquots from the reacting solution were quenched by pouring them into the columns followed by 10 ml. of anhydrous benzene. The first 4 ml. of eluate was discarded (approximately the solvent capacity of the resin) then 7 ml. was collected and finally the last 4 ml. discarded. To the middle 7 ml. which had been collected 50 ml. of 95% ethanol was added and then 10 ml. of 0.03 *N* alcoholic silver nitrate, which precipitated the chlorine as silver chloride. These samples were dried under vacuum, weighed into brass boats, and counted in a "nucleometer" which has been described elsewhere.[36]

When this work was begun (in cool weather) it was found that, for a given sample, the number of counts per min. per mg. was approximately independent of the weight of sample between 8 and 28 mg. Furthermore, the deviations were a linear function of the weight of sample so that a 1.06% per mg. correction would permit the conversion of any value for weights within this range to that for any other weight. Accordingly the total yield of silver chloride (10–24 g., 40–100%) was weighed, counted, and the counts per min. per mg. value converted to a common weight before the percentage reaction was calculated. Later, when the weather became hot and humid a much larger correction factor was indicated, so it was thought better to level the samples to a common weight before counting. Infinity points were obtained by adding alcohol directly to portions of the reaction mixture, then proceeding as above.

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[35] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 969 (1949).

[36] C. C. Lee, Sc.D. thesis, M.I.T., February, 1952, p. 31.