handled in the usual manner to recover caproic acid and the water-soluble acid.

Chromotropic acid[10] was used to test for formic acid which might have been formed if sodium hydride were produced by pyrolysis, but none was found. Neither was oxalic acid detectable by the use of diphenylamine.[10]

Any tertiary alkoxide used in the work was prepared and added in the manner described in the previous paper[8] and any variation from the conditions given above are indicated in the table.

In all these experiments the propeller blades were three oblique discs approximately $2^{1}/_{8}''$ long by $^{11}/_{16}''$ at the widest point each welded at the center of the straight edge into a slot in the end of the $^{3}/_{8}''$ shaft so that the blades were at a 45° angle from the shaft. This sturdier type of agitator has been used for approximately the last two years in this program of research and gives the excellent agitation needed in much of this work, particularly with granular salts.

**Examination of the High-boiling Material.**—This material, which was originally collected from 170 to 265°, was refractionated twice in order to collect concentrates of compounds that might be present. Out of 20 g. about 3 g. of material proved to be decane. One fraction (2.3 g.) was reasonably pure di-*n*-amyl ketone, as shown by its identity with an authentic sample in boiling point (55.5° (19 mm.)), refractive index ($n^{25}$D 1.4250) and the yellow *p*-nitrophenylhydrazone derivative (m.p. 67–88°, reported[11] 68°) which readily decomposed to a red oil on standing overnight. Another fraction (1.2 g.) was largely triamylcarbinol, as judged by the refractive index $n^{25}$D 1.4453 (reported[12] $n^{20}$D 1.4470 and boiling point 104° (1 mm.)). Several fractions amounting to 3.7 g. gave a material that boiled 77.5–79.0° (0.15 mm.) and decolorized bromine. All fractions and compounds were analyzed for carbon and hydrogen and found to agree with the formula assigned. These examinations were sufficient to show that the high-boiling material was not derived by polymerization of amyl radicals.

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[10] F. Feigl, "Quantitative Analysis by Spot Tests," 3rd Ed., Trans. by R. E. Oesper, Elsevier Publishing Co., Inc., New York, N. Y., 1946.

[11] A. D. Petrov and E. P. Kaplan, *Izvest. Akad. Nauk U.S.S.R. Otdel Khim. Nauk*, **539** (1949); *C. A.*, **44**, 1887 (1950).

[12] F. C. Whitmore and F. E. Williams, THIS JOURNAL, **55**, 406 (1933).

CAMBRIDGE 39, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Kinetic Evidence for the Triphenylcarbonium Ion as a Reaction Intermediate and Measurement of its Relative Reactivity with Seven Nucleophilic Reagents[1]

BY C. GARDNER SWAIN, CARLETON B. SCOTT AND KARL H. LOHMANN

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Exceptionally clear evidence for the existence of a carbonium ion intermediate appears in the hydrolysis of $10^{-3}$ *M* triphenylmethyl (trityl) fluoride, chloride, bromide or thiocyanate in water–acetone solutions. When $10^{-3}$ *M* azide ion (a strong nucleophilic reagent) is added to any one of these, the rate is unaffected but the product is changed from 100% trityl alcohol to 90% trityl azide. When $10^{-2}$ *M* chloride ion is added to a $10^{-3}$ *M* solution of either trityl chloride or bromide, the rate is reduced ("mass effect") to 25% of the rate with trityl chloride alone. By competition experiments, the relative reactivities (*vs.* water) of seven different nucleophilic reagents toward trityl ion have been measured. Trityl ion discriminates much more highly between different nucleophilic reagents than carbonium ions which have a more localized positive charge. Some of the measured relative reactivities are $3.1 \times 10^{3}$ (dimensionless ratio) for chloride ion, $3.7 \times 10^{3}$ for aniline, $5.3 \times 10^{4}$ for hydroxide ion and $2.8 \times 10^{5}$ for azide ion. These figures were affected only slightly by per cent. acetone in the water, temperature and source of trityl ion (from trityl fluoride, chloride or thiocyanate).

Triphenylmethyl (trityl) fluoride liberates fluoride ion in 50% water–50% acetone solution at 25° with a first-order constant ($7.6 \pm 0.4 \times 10^{-4}$ sec.$^{-1}$) *independent* of the concentrations of trityl fluoride ($10^{-3}$ to $10^{-2}$ *M*) or added sodium fluoride (0 to $3 \times 10^{-3}$ *M*), sodium hydroxide (0 to $5 \times 10^{-3}$ *M*), nitric acid (0 to $5 \times 10^{-3}$ *M*) or sodium azide (0 to $3 \times 10^{-3}$ *M*). In the absence of added salts, both acid and fluoride ion are produced in 100% yield based on the initial molarity of trityl fluoride, and both are formed at the same rate within the experimental error.

Although the rate is not affected by sodium azide, the product composition is. Adding as little as $1.3 \times 10^{-3}$ *M* sodium azide decreases to 9.8% the total acid produced indicating the formation of 90% trityl azide. From a reaction with $2 \times 10^{-1}$ *M* sodium azide, trityl azide, m.p. 58–60°, was isolated in 97% yield. These results can be interpreted only by postulating an unstable intermediate (I) for which water and added anions compete.

$$(C_6H_5)_3CF \xrightarrow[7.6 \times 10^{-4}\ \text{sec.}^{-1}]{k_1,\ \text{slow}} \text{I}$$

$$\text{I} - \begin{cases} \xrightarrow{k,\ Y^-,\ \text{fast}} (C_6H_5)_3Y + F^- \\ \xrightarrow{k^\circ,\ H_2O,\ \text{fast}} (C_6H_5)_3COH + H_3O^+ + F^- \end{cases}$$

Here $Y^-$ may be $N_3^-$, $HO^-$, or any nucleophilic reagent capable of yielding a stable product and $k^\circ$ and $k$ are both large second-order rate constants.

It is quite reasonable to write I as

$$(C_6H_5)_3C^{\oplus} + F^{\ominus} \text{ (both ions solvated)}$$

and it is probable in this highly aqueous medium that the ions are dissociated, *i.e.*, that trityl ion is symmetrically solvated by water molecules at the stage where competition with nucleophilic reagents like azide ion occurs.

When only water and azide ion are present

$$\frac{d[(C_6H_5)_3CN_3]}{d[(C_6H_5)_3COH]} = \frac{k_{N_3^-}[N_3^-]}{k^\circ[H_2O]}$$

Integration gives $k_{N_3^-}/k^\circ = ([H_2O]/x) \ln [b/(b - a + x)]$ where $b$ is the initial concentration of azide ion, $a$ is the initial concentration of trityl compound and $x$ is the concentration of acid liberated after ten half-lives.

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[1] This work was supported by the Office of Naval Research, contract no. N5-ori-07838, project no. NR056-198. For full experimental data for runs in 6% water, see K. H. Lohmann, S. B. thesis, M.I.T., May, 1950; for other solvents, see C. B. Scott, Ph.D. thesis, M.I.T., January, 1952.

The dimensionless rate constant ratio $k_{N_3^-}/k^\circ$ is 2.8 × $10^5$ using trityl fluoride in 50% water–50% acetone at 25°. Similar values were found with trityl fluoride in 20% water–80% acetone at 25° (2.4 × $10^5$), trityl chloride in 15% water–85% acetone at −34° (1.1 × $10^5$), or 6% water–2% dioxane–92% acetone at 25° (0.9 × $10^5$), or trityl thiocyanate in 50% water–50% acetone at 25° (3.1 × $10^5$). The mean of all of these is 2.1 × $10^5$ and the average deviation is a factor of only 1.8. The variation is probably chiefly due to a slightly higher nucleophilic reactivity for water (higher $k^\circ$) because of less self-association of the water by hydrogen bonding in the media in which water is less concentrated.

When hydroxide ion is also present at an initial concentration of $c$

$$\frac{d[(C_6H_5)_3CN_3]}{d[(C_6H_5)_3COH]} = \frac{k_{N_3^-}[N_3^-]}{k^\circ[H_2O] + k_{OH^-}[OH^-]}$$

Integration gives

$$\ln\left(\frac{[H_2O] + KK'c}{[H_2O] + KK'(c - x)}\right) = K' \ln\left(\frac{b}{b - a + x}\right)$$

where $K = k_{N_3^-}/k^\circ$ (evaluated previously), $K' = k_{OH^-}/k_{N_3^-}$ and the other symbols were defined previously. Then $k_{OH^-}/k^\circ = KK'$.

Trityl chloride ($10^{-3}$ $M$) hydrolyzed much faster than trityl fluoride, but could be followed in 15% water–85% acetone at −34°. Adding $10^{-2}$ $M$ sodium chloride decreased the rate by a factor of four, indicating that chloride ion competed for the carbonium ion, diverting part of it back to trityl chloride.

$$\begin{tikzcd}
(C_6H_5)_3CCl \arrow[r, shift left, "k_1\text{, slow}"] & (C_6H_5)_3C^+ + Cl^- \arrow[l, shift left, "k_{Cl^-}\text{, fast}"] \arrow[d, "k^\circ"', "H_2O\text{, fast}"] \\
 & (C_6H_5)_3COH + H_3O^+
\end{tikzcd}$$

From this "mass effect" of chloride ion on the rate, $k_{Cl^-}/k^\circ$ was calculated.

$$d[H_3O^+]/dt = k^\circ[(C_6H_5)_3C^+][H_2O]$$

and

$$[(C_6H_5)_3C^+] = \frac{k_1[(C_6H_5)_3CCl]}{k_{Cl^-}[Cl^-] + k^\circ[H_2O]}$$

Hence the ratio of rates without and with added chloride ion equals $1 + K_{Cl^-}[Cl^-]/k^\circ[H_2O]$, and $k_{Cl^-}/k^\circ$ can be calculated. In the runs without added chloride, perchlorate ion was added to maintain the same ionic strength.

Table I lists relative reactivities for seven nucleophilic reagents toward trityl ion and compares them with relative reactivities toward $p,p'$-dimethylbenzhydryl ion, benzhydryl ion and $t$-butyl ion. Most of the data on benzhydryl ion were also determined in the course of the present study.

The relative reactivity, $k_{N_3^-}/k^\circ$, increases from 3.9 for $t$-butyl ion to 170 for benzhydryl ion, to 240 for $p,p'$-dimethylbenzhydryl ion, to 280,000 for trityl ion. Thus trityl ion appears to discriminate more highly than the carbonium ions which have a more concentrated charge. This may be due to its higher stability, which allows more trial collisions with different possible reactants to occur.

TABLE I

RELATIVE REACTIVITIES ($k/k^\circ$) OF NUCLEOPHILIC REAGENTS TOWARD CARBONIUM IONS

| Nucleophilic reagent | $(C_6H_5)_3C^+$ | $(p\text{-}CH_3C_6H_4)_2\text{-}CH^+$ | $(C_6H_5)_2\text{-}CH^+$ | $(CH_3)_3C^+$ |
|---|---|---|---|---|
| $H_2O$ | 1 | 1 | 1 | 1 |
| $CH_3COO^-$ | 1.1 × $10^{3a}$ | ........ | ........ | ........ |
| $Cl^-$ | 3.1 × $10^{3b}$ | 6.0 × $10^{2e}$ | 1.2 × $10^{2g}$ | 1.8 × $10^{2j}$ |
| $Br^-$ | ........ | ........ | 3.3 × $10^{2h}$ | ........ |
| $C_6H_5NH_2$ | 3.7 × $10^{3a}$ | ........ | ........ | ........ |
| $N_3^-$ | 2.8 × $10^{5c}$ | 2.4 × $10^{2f}$ | 1.7 × $10^{2i}$ | 3.9$^k$ |
| $HO^-$ | 5.3 × $10^{4c}$ | ........ | 7.7 × $10^{3i}$ | ........ |
| $SCN^-$ | 1.3 × $10^{4a}$ | ........ | ........ | ........ |
| $S_2O_3^-$ | 1.9 × $10^{4c}$ | ........ | ........ | 3.4 × $10^{2j}$ |

[a] From trityl chloride in 6% water–2% dioxane–92% acetone at 25°. [b] From trityl chloride in 15% water–85% acetone at −34°. [c] From trityl fluoride in 50% water–50% acetone at 25°. Other values for $N_3^-$ are 0.9 × $10^5$,[a] 1.1 × 10,[5b] and 2.4 × $10^{5d}$; for $HO^-$, 9.7 × $10^{3a}$; for $S_2O_3^=$, 3.1 × 10.[3a] [d] From trityl fluoride in 20% water–80% acetone at 25°. [e] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940); from $p,p'$-dimethylbenzhydryl chloride in 15% water–85% acetone at 0°. [f] L. C. Bateman, E. D. Hughes and C. K. Ingold, *ibid.*, 974 (1940); from $p,p'$-dimethylbenzhydryl chloride in 10% water–90% acetone at 0°. Another value for $N_3^-$ in 20% water–80% acetone at 0° is 4.7 × $10^2$. [g] *Ibid.*, from benzhydryl chloride in 20% water–80% acetone at 25°. [h] *Ibid.*, from benzhydryl bromide in 10% water–90% acetone at 50°. [i] From benzhydryl bromide in 30% water–70% acetone at 25°. Other values for $N_3^-$ are 2 × $10^2$ in 10% water–90% acetone at 25° and 1.8 × $10^2$ in the same solvent at 50°. [j] A. G. Ogston, E. R. Holiday, J. St. L. Philpot and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948); in 95% water–5% ethanol at 25°. [k] L. C. Bateman, E. D. Hughes and C. K Ingold, *J. Chem. Soc.*, 960 (1940); in 10% water–90% acetone at 50°.

## Experimental

**Reagents.**—All melting points are corrected, all boiling points are uncorrected.

Trityl fluoride was usually prepared by placing approximately 25 g. of trityl chloride in a copper cell, fitted with polyethylene liner and nickel stirrer and passing in anhydrous hydrogen fluoride gas (Matheson 99% pure) for about 1 hr. while the cell stood in an ice-bath. After addition of the hydrogen fluoride, the ice-bath was replaced by a steam-bath for 2 hr. to remove the excess hydrogen fluoride. The dark liquid in the cell was then transferred to a stainless steel beaker and heated to dryness on a hot-plate. Benzene, usually 100 ml., was added during the final heating to facilitate the removal of residual hydrogen fluoride. After cooling, the crude trityl fluoride was recrystallized from anhydrous ether at Dry Ice temperatures. Most of the residual hydrogen fluoride and solvent could be removed by storing the product in a desiccator containing Drierite, potassium hydroxide flakes and paraffin chips. The usual yield was about 60% of a product containing 85–95% trityl fluoride, m.p. 102.4–103.4°.[2] The impurity was triphenylcarbinol, which did not interfere with the kinetic measurements.

Trityl chloride was prepared according to Bachmann.[3] The yield from 50 g. of triphenylcarbinol, m.p. 160–161°, was 40 g. (75%), m.p. 111–112°. Recrystallization from benzene and petroleum ether gave the product used in the kinetic runs, m.p. 111.9–112.4°.

Trityl thiocyanate was prepared in 60% yield by the method of Billmann and Due,[4] except that sodium thiocyanate was substituted for ammonium thiocyanate. The product was recrystallized from benzene and $n$-hexane, m.p. 137.8–138.4°.

Trityl bromide was prepared from triphenylcarbinol and dry hydrogen bromide gas and recrystallized several times from benzene, m.p. 153–155°.

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(2) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949), reported m.p. 102–103.°

(3) W. E. Bachmann, *Org. Syntheses*, **23**, 99 (1943).

(4) E. Billmann and N. V. Due, *Bull. soc. chim.* [*France*], [4] **35**, 384 (1924).

Trityl benzoate was prepared from silver benzoate and trityl chloride.[5] Silver benzoate (20.7 g., 0.09 mole) was placed in 400 ml. of benzene and 100 ml. distilled to dry the silver benzoate. Trityl chloride (8.4 g., 0.03 mole) was added in 50 ml. of benzene and the mixture refluxed for 20 hr. The silver chloride was removed by filtration and washed with ether. The ether and benzene solutions were combined, evaporated almost to dryness and the trityl benzoate caused to crystallize by the addition of *n*-hexane. The yield was 11 g. (100%), m.p. 171.4–172.4°.

Trityl acetate was prepared from trityl chloride and silver acetate[6] in a manner similar to that used for trityl benzoate, 44% yield, m.p. 84–85°, 98.8% pure based on acid produced on hydrolysis.

Benzhydryl bromide was prepared from benzhydrol and phosphorus tribromide.[7] Benzhydrol (86.2 g., 0.47 mole, m.p. 65–66°) was dissolved in 400 ml. of carbon tetrachloride and 60 g. (0.22 mole) of phosphorus tribromide in 100 ml. of carbon tetrachloride was added over a period of two hours with stirring. The reaction was conducted in a 1000-ml. flask fitted with mercury-sealed stirrer, condenser and protected from moisture by calcium chloride tubes. The reaction mixture was allowed to stand for 24 hr., then heated to 60–70° for 6 hr. A yellow residue was removed by filtration and the carbon tetrachloride solution was washed twice with 300 ml. of ice-water, twice with 300 ml. of 0.5 $M$ cold sodium acetate solution, then dried over potassium carbonate for 12 hr. The crude benzhydryl bromide, 79.7 g. (69%), b.p. 135–141° (3 mm.), was fractionally distilled. The sample used for kinetic studies had b.p. 144–145° (3 mm.), $n^{25}{}_{D}$ 1.6197.

Sodium azide was Eastman Kodak Co. practical grade, recrystallized from acetone and water and stored in a desiccator over Drierite.

Aniline was redistilled from zinc dust immediately before use, b.p. 184–185°.

Acetone was Mallinckrodt "Analytical Reagent" dried over Drierite for at least a week and distilled through a dry apparatus immediately before use. Dioxane was purified by refluxing with hydrochloric acid[8] and stored over sodium wire in a dark bottle,

**Product Isolation.**—Trityl azide was isolated in good yield from the reaction with sodium azide. Sodium azide (1.63 g., 0.025 mole) in 130 ml. of water was added to a solution of 2.5 g. (0.0083 mole) of trityl thiocyanate in 200 ml. of acetone. After 24 hr., 250 ml. of water was added, the solution was extracted three times with ether and once with benzene, the combined extracts dried over sodium sulfate and evaporated almost to dryness. Addition of 10 ml. of acetone and some water, followed by cooling, yielded 2.2 g. (97%) of trityl azide, m.p. 58–60°. Two recrystallizations from acetone and water give 1 g., m.p. 64.5–65.5°.[9]

**Kinetic Procedure.**—Temperature control was ±0.01° at 49.8°, 25° and 20°, ±0.5° at 0° and below.

Most of the hydrolyses of trityl and benzhydryl halides were conducted in an apparatus and by a procedure which has been described previously.[10] The liberated acid was titrated with 0.05 $M$ carbonate-free sodium hydroxide for runs at 25 and 49.8° or with 0.09 $M$ triethylamine in 15% water–85% acetone for runs at −14° or −34°. Brom thymol blue was the indicator except for low temperature hydrolyses where brom cresol green proved more satisfactory. A 5-ml. microburet graduated in 0.01 ml. was used. At 49.8° it was necessary to run the reactions in glass-stoppered flasks due to the high vapor pressure of the solvent at that temperature. For some very slow reactions of trityl fluoride, polyethylene bottles were used to prevent etching of the glass. Half-lives were determined by plotting per cent. reaction *vs.* time on semi-logarithmic paper and drawing the best straight line through the points. The rate constant was taken as 0.693 divided by the time difference on this line between 0–50% reaction.

When the trityl or benzhydryl halides were allowed to react in the presence of salts, a 100-ml. round bottomed flask equipped with sealed stirrer and glass-stoppered side arm was used. These reactions were followed by extracting aliquots with benzene or chloroform and titrating the aqueous portions for halide ion. Benzene was used when fluoride ion was being liberated or when perchlorate ion was present since chloroform is less satisfactory under these conditions. Fluoride ion was titrated at $p$H 3 with 0.05 $N$ thorium nitrate,[11] using 5 drops of 1% sodium alizarinsulfonate and 1 drop of 1% methylene blue. The end-point was a change from green to gray-purple. This analytical method was used for runs 81–97, inclusive. It gave rate constants agreeing with those from runs followed by titration with sodium hydroxide within the experimental error.[2] However, the fluoride method appeared to be more accurate than the acidimetric method whenever trityl fluoride was used in media containing 50% or more of acetone. It avoided difficulties in the acidimetric methods caused by buffering and slightly changing water concentration from addition of titrating solution. Chloride ion and bromide ion were titrated at $p$H 3 with 0.05 $N$ mercuric nitrate[12] using 5 drops of 1% ethanolic diphenylcarbazide. The end-point was a change from colorless to purple. This analytical method was used for runs 177–196, inclusive.

The same apparatus was used for competition experiments as was used for the kinetic experiments. To determine the reactivity of azide ion, the solvent, less 5 or 10 ml. of acetone, but containing sodium azide and brom thymol blue, was placed in the cell and nitrogen bubbled through the solution with good stirring until the indicator turned to its neutral color. Then the trityl or benzhydryl halide was added in the 5 or 10 ml. of acetone, which brought the solvent to

Table II

Sample Kinetic Data in Aqueous Acetone Solutions

| Source of $(C_6H_5)_3C^+$ | Concn., $M$ × $10^3$ | Water, % by volume | Temp., °C. | Added reagent | Concn., $M$ × $10^3$ | $k_1$, sec.$^{-1}$ | Run no. |
|---|---|---|---|---|---|---|---|
| Trityl fluoride | 1.04 | 50 | 25 | .... | .. | $7.7 \times 10^{-4}$ | 81 |
| | 1.01 | 50 | 25 | $NaN_3$ | 3.31 | $7.4 \times 10^{-4}$ | 83 |
| | 8.41 | 50 | 25 | $HNO_3$<br>NaF | 4.92<br>2.99 | $7.5 \times 10^{-4}$ | 98 |
| | 8.50 | 50 | 25 | $HNO_3$ | 4.92 | $7.5 \times 10^{-4}$ | 99 |
| | 8.54 | 50 | 25 | NaOH<br>$NaN_3$ | 2.50<br>2.52 | $7.9 \times 10^{-4}$ | 96 |
| | 8.33 | 50 | 25 | NaOH<br>NaF | 5.00<br>3.10 | $7.2 \times 10^{-4}$ | 97 |
| Trityl thiocyanate | 0.79 | 50 | 25 | .... | .. | $2.2 \times 10^{-3}$ | 28 |
| | 1.0 | 6 | 25 | .... | .. | $2.4 \times 10^{-4}$ | ... |
| Trityl chloride | 1.09 | 15 | −33.0 | .... | .. | $1.7 \times 10^{-2}$ | 130 |
| | 0.55 | 15 | −34.5 | .... | .. | $1.3 \times 10^{-2}$ | 131 |
| | 1.40 | 15 | −14.0 | .... | .. | $1.1 \times 10^{-1}$ | 146 |
| | 1.29 | 15 | −34.5 | KCl | 10 | $3.8 \times 10^{-3}$ | 132 |
| | 1.44 | 15 | −34.2 | KCl | 8 | $4.3 \times 10^{-3}$ | 144 |
| | 1.15 | 15 | −33.5 | $KNO_3$ | 10 | $1.8 \times 10^{-2}$ | 133 |
| | 1.42 | 15 | −35.0 | $KNO_3$ | 8 | $1.7 \times 10^{-2}$ | 145 |
| | 0.86 | 15 | −35.0 | $KClO_4$ | 10 | $1.8 \times 10^{-2}$ | 134 |
| | 1.44 | 15 | −34.0 | $NaN_3$ | 3 | $1.7 \times 10^{-2}$ | 136 |
| | 1.40 | 15 | −34.0 | KBr | 10 | $1.8 \times 10^{-2}$ | 139 |
| | 1.34 | 15 | −34.2 | LiBr | 10 | $1.8 \times 10^{-2}$ | 143 |
| | 1.44 | 15 | −34.0 | NaF | 4 | $1.6 \times 10^{-2}$ | 142 |
| Trityl bromide | 1.32 | 15 | −34.5 | KCl | 10 | $3.8 \times 10^{-3}$ | 140 |
| | 1.32 | 15 | −34.5 | LiBr | 10 | $>3 \times 10^{-2}$ | 141 |
| Trityl benzoate | 0.49 | 50 | 25 | .... | .. | $1.2 \times 10^{-3}$ | 57 |
| | 0.99 | 40 | 25 | .... | .. | $4.1 \times 10^{-4}$ | 55 |
| Trityl acetate | 0.99 | 50 | 25 | .... | .. | $7.2 \times 10^{-4}$ | 58 |
| Benzhydryl chloride | 2.19 | 50 | 25 | .... | .. | $1.6 \times 10^{-2}$ | 172 |
| | 2.73 | 50 | 25 | .... | .. | $1.7 \times 10^{-2}$ | 173 |
| Benzhydryl bromide | 2.58 | 10 | 25 | .... | .. | $1.8 \times 10^{-4}$ | 202 |
| | 1.52 | 30 | 25 | .... | .. | $1.2 \times 10^{-2}$ | 175 |
| | 10.3 | 30 | 25 | $LiClO_4$ | 100 | $1.3 \times 10^{-2}$ | 177 |
| | 11.9 | 30 | 25 | $HClO_4$ | 100 | $1.4 \times 10^{-2}$ | 178 |
| | 8.6 | 30 | 25 | $NaN_3$ | 100 | $1.3 \times 10^{-2}$ | 195 |
| | 9.6 | 30 | 25 | NaOH | 20 | $1.3 \times 10^{-2}$ | 196 |

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[9] H. Wieland, *Ber.*, **42**, 3027 (1909), reported m.p. 65°.

[10] Method D used by C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, This Journal, **71**, 969 (1949).

[11] H. Ballczo, *Österr. Chem. Z.*, **50**, 146 (1949); *C. A.*, **43**, 8960 (1949).

[12] I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

TABLE III

SUMMARY OF COMPETITION EXPERIMENTS

| Source of ion (I) | Concn., $M \times 10^3$ | Solvent, % | Temp., °C. | Added reagents | Concn., $M \times 10^3$ | $k/k_{\mathrm{w}}$ | $k/k^{d}$ | Total no. of experiments averaged |
|---|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3CF$ | 1.22 | 20 water<br>80 acetone | 25 | $NaN_3$ | 4.00 | $k_{\mathrm{N_3^-}}/k_{\mathrm{w}} = 22,000$ | $2.4 \times 10^5$ | 3 |
| | 0.80 | 50 water<br>50 acetone | 25 | $NaN_3$ | 1.3–2.5 | $k_{\mathrm{N_3^-}}/k_{\mathrm{w}} = 10,000$ | $2.8 \times 10^5$ | 13 |
| | .80 | 50 water<br>50 acetone | 25 | $NaN_3$<br>NaOH | 1.2–2.5<br>1.0–2.0 | $k_{\mathrm{N_3^-}}/k_{\mathrm{HO^-}} = 5.3$ | | 8 |
| | | 50 water<br>50 acetone | 25 | | | $k_{\mathrm{HO^-}}/k_{\mathrm{w}} = 1900$ | $5.3 \times 10^4$ | |
| | 1.12 | 50 water<br>50 acetone | 25 | $Na_2S_2O_3$ | 2.0 | $k_{\mathrm{S_2O_3^{=}}}/k_{\mathrm{w}} = 700$ | $1.9 \times 10^4$ | 3 |
| $(C_6H_5)_3CSCN$ | 0.78 | 50 water<br>50 acetone | 25 | $NaN_3$ | 1.0–1.8 | $k_{\mathrm{N_3^-}}/k_{\mathrm{w}} = 11,000$ | $3.1 \times 10^5$ | 12 |
| | .75– .79 | 50 water<br>50 acetone | 25 | $NaN_3$<br>NaOH | 0.8–2.0<br>1.0–2.5 | $k_{\mathrm{N_3^-}}/k_{\mathrm{HO^-}} = 6.3$ | | 11 |
| | | 50 water<br>50 acetone | 25 | | | $k_{\mathrm{HO^-}}/k_{\mathrm{w}} = 1750$ | $4.9 \times 10^4$ | |
| $(C_6H_5)_3CCl$ | 1.40 | 15 water<br>85 acetone | −34 | $NaN_3$ | 1.5–3.0 | $k_{\mathrm{N_3^-}}/k_{\mathrm{w}} = 13,000$ | $1.1 \times 10^5$ | 3 |
| | 0.99 | 6 water<br>2 dioxane<br>92 acetone | 25 | $NaN_3$ | 1.0–2.0 | $k_{\mathrm{N_3^-}}/k_{\mathrm{w}} = 27,000$ | $9.0 \times 10^4$ | 16 |
| | 0.97 | 6 water<br>2 dioxane<br>92 acetone | −25 | $NaN_3$<br>NaOH | 1.0–2.0<br>0.5–1.2 | $k_{\mathrm{N_3^-}}/k_{\mathrm{HO^-}} = 9.3$ | | 20 |
| | | 6 water<br>2 dioxane<br>92 acetone | 25 | | | $k_{\mathrm{HO^-}}/k = 2900$ | $9.7 \times 10^3$ | |
| | 0.96 | 6 water<br>2 dioxane<br>92 acetone | 25 | $NaN_3$<br>$C_6H_5NH_2$ | 1.0–2.0<br>20–40 | $k_{\mathrm{N_3^-}}/k_{\mathrm{aniline}} = 24$ | | 7 |
| | | 6 water<br>2 dioxane<br>92 acetone | 25 | | | $k_{\mathrm{aniline}}/k_{\mathrm{w}} = 1100$ | $3.7 \times 10^3$ | |
| | .96 | 6 water<br>2 dioxane<br>92 acetone | 25 | NaSCN | 1.0–3.0 | $k_{\mathrm{SCN^-}}/k_{\mathrm{w}} = 3900$ | $1.3 \times 10^4$ | 9 |
| | .32 | 6 water<br>2 dioxane<br>92 acetone | 25 | $Na_2S_2O_3$ | 0.16–0.33 | $k_{\mathrm{S_2O_3^{=}}}/k_{\mathrm{w}} = 930$ | $3.1 \times 10^3$ | 11 |
| | .98 | 6 water<br>2 dioxane<br>92 acetone | 25 | NaOAc | 2.5–7.5 | $k_{\mathrm{AcO^-}}/k_{\mathrm{w}} = 330$ | $1.1 \times 10^3$ | 15 |
| $(C_6H_5)_2CHBr$ | $1.5\text{–}2.0 \times 10^{-3}$ | 30 water<br>70 acetone | 25 | $NaN_3$ | 20 | $k_{\mathrm{N_3^-}}/k_{\mathrm{H_2O}} = 10$ | $1.7 \times 10^2$ | 6 |
| | $1.3\text{–}1.7 \times 10^{-3}$ | 30 water<br>70 acetone | 25 | $NaN_3$<br>NaOH | 40<br>2 | $k_{\mathrm{N_3^-}}/k_{\mathrm{HO^-}} = 0.022$ | | 4 |
| | | 30 water<br>70 acetone | 25 | | | $k_{\mathrm{HO^-}}/k_{\mathrm{H_2O}} = 460$ | $7.7 \times 10^3$ | |
| | $1.0 \times 10^{-3}$ | 10 water<br>90 acetone | 25 | $NaN_3$ | 40 | $k_{\mathrm{N_3^-}}/k_{\mathrm{H_2O}} = 36$ | $2.0 \times 10^2$ | 3 |
| | $1.3 \times 10^{-3}$ | 10 water<br>90 acetone | 50 | $NaN_3$ | 40 | $k_{\mathrm{N_3^-}}/k_{\mathrm{H_2O}} = 32$ | $1.8 \times 10^2$ | 2 |

the proper proportions. The final volume was 100 ml. on an unmixed basis.

After a period of time corresponding to ten half-lives for the solvolysis of the trityl or benzhydryl halide under these conditions, the amount of triphenylcarbinol or benzhydrol was determined by titrating for liberated acid. The concentration of trityl or benzhydryl azide was determined by difference from the original concentration of the organic halide and the final concentration of carbinol. This was possible since the organic azides were inert to hydrolysis under these conditions. A similar procedure was used to determine the relative reactivities of azide ion and hydroxide ion, the only difference being that sodium hydroxide was added with the sodium azide and the final reaction mixture titrated for unreacted hydroxide ion with standard acid. The standard bases were 0.05 and 0.1 *N* sodium hydroxide for the runs at 25 and 49.8° and the standard base for runs at −34° was 0.02636 *N* tetraethylammonium hydroxide in 15% water–85% acetone.

When thiocyanate ion was used, a correction was made for the amount of trityl thiocyanate which hydrolyzed during the run.

Since hydrazoic acid is a weak acid, it was necessary to correct for the acid consumed by unreacted sodium azide in the runs in 50% water–50% acetone. The corrections were determined by noting the amount of acid required to neutralize varying amounts of sodium azide placed in a neutral solution. This difficulty did not arise in solutions containing less water.

For the runs in 6% water–92% acetone–2% dioxane, a fresh stock solution of 0.05 *M* trityl chloride in dioxane was made each day. With only 6% water at 25°, the results from competition experiments were independent of the rate of addition of the trityl chloride solution or the rate of stirring. However, with trityl chloride in 15% water–83% acetone–2% dioxane at 25° the titers varied up to 500% depending on the time of addition and motor speed, because the high speed of reaction did not permit proper mixing before reaction and a local deficiency of the nucleophilic solute (*e.g.*, azide ion) developed. The lower (6%) water concentration was also advantageous in preventing or minimizing hydrolysis of the products prior to titration.

TABLE IV

REACTION OF TRIPHENYLMETHYL FLUORIDE IN THE PRESENCE OF SODIUM AZIDE IN 50% WATER–50% ACETONE AT 25°

| Run | $NaN_3$ initial, $M \times 10^4$ | $(C_6H_5)_3CF$ initial, $M \times 10^4$ | $(C_6H_5)_3$-$CN_3$ final, $M \times 10^4$ | $(C_6H_5)_3$-COH final, $M \times 10^4$ | $k_{N_3^-}/k^0 \times 10^{-5}$ |
|---|---|---|---|---|---|
| 7 | 18.5 | 9.21 | 8.59 | 0.62 | 2.81 |
| 8 | 18.5 | 9.92 | 9.37 | .55 | 3.56 |
| 12 | 18.5 | 10.22 | 9.46 | .76 | 2.61 |
| 13 | 10.2 | 8.96 | 7.25 | 1.71 | 2.00 |
| 14 | 10.2 | 9.05 | 7.28 | 1.77 | 1.97 |
| 15 | 18.5 | 9.05 | 8.57 | 0.48 | 3.70 |
| 16 | 12.0 | 9.05 | 7.80 | 1.25 | 2.33 |
| 17 | 13.9 | 9.05 | 8.20 | 0.85 | 2.89 |
| 19 | 15.7 | 9.05 | 8.35 | .70 | 3.00 |
| 84 | 12.88 | 7.93 | 7.15 | .78 | 2.89 |
| 85 | 25.60 | 8.10 | 7.73 | .37 | 2.72 |
| 86 | 16.90 | 7.95 | 7.45 | .50 | 3.20 |
| 87 | 20.60 | 8.00 | 7.59 | .42 | 3.08 |
| | | | | Mean | 2.8 |

In all cases, the concentration (*M*) of water present was used in calculating $k/k^0$ values. All concentrations were based on volumes prior to mixing.

An attempt was made to determine the reactivity of bromide ion but even with a ten-fold excess of bromide ion in 15% water–85% acetone at −34°, trityl bromide hydrolyzed much too rapidly to follow. It was interesting to note, however, that trityl bromide and trityl chloride hydrolyzed at the same rate when a ten-fold excess of chloride ion was present, thus indicating complete capture of the trityl ion from trityl bromide by chloride ion to regenerate trityl chloride.

The kinetic measurements are summarized in Table II, the competition experiments in Table III, and details of typical runs are given in Tables IV and V.

TABLE V

RUN 144 HYDROLYSIS OF $1.44 \times 10^{-3}$ *M* TRIPHENYLMETHYL CHLORIDE IN THE PRESENCE OF 0.008 *M* POTASSIUM CHLORIDE IN 15% WATER–85% ACETONE AT −34.2°

$t_{1/2}$ = 160 sec., mean $k_1 = 4.35 \pm 0.04 \times 10^{-3}$ sec. $^{-1}$

| Time, sec. | 0.0911 *M* $(C_2H_5)_3N$, ml. | $H_3O^+$ liberated, % of $1.44 \times 10^{-3}$ *M* | $k_1 \times 10^3$ sec. $^{-1}$ |
|---|---|---|---|
| 0 | .. | .. | .. |
| 6 | 0.04 | 2.6 | (4.42) |
| 18 | .11 | 7.2 | (4.18) |
| 36 | .22 | 14.5 | 4.35 |
| 57 | .33 | 21.7 | 4.30 |
| 73 | .42 | 27.6 | 4.43 |
| 93 | .51 | 33.6 | 4.40 |
| 129 | .65 | 42.7 | 4.33 |
| 171 | .80 | 52.6 | 4.38 |
| 248 | 1.00 | 65.8 | 4.34 |
| 298 | 1.10 | 72.4 | 4.32 |
| 362 | 1.20 | 78.9 | 4.31 |
| 448 | 1.30 | 85.5 | 4.32 |
| 508 | 1.35 | 88.8 | 4.32 |
| 1800 | 1.52 | 100 | .. |

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