[Contribution from the Department of Chemistry and the Laboratory for Nuclear Science, Massachusetts Institute of Technology]

Mechanism of Methanolysis of Triphenylmethyl Chloride in Benzene Solution[1-3]

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The methanolysis of 0.1 M triphenylmethyl (trityl) chloride in benzene solution at 25° has been studied from 5×10^{-2} M methanol down to the very low concentration of 5×10^{-7} M methanol by a tracer technique specific for the methanolysis reaction. The rate is practically independent of the nature or concentration of tertiary amine used to bind the hydrogen chloride produced. The total kinetic order decreases from approximately third order at 5×10^{-2} M methanol to second order at 10^{-3} M; below 10^{-3} M methanol it remains second order over-all (first order in both trityl chloride and methanol). These observations plus Kreevoy's earlier work on exchange with quaternary ammonium salts demonstrate that the mechanism below 10^{-3} M methanol is a reversible ionization of trityl chloride assisted by only the solvent benzene, followed by a rate-determining reaction of triphenylcarbonium chloride with methanol. The deuterium isotope effect k_{CH_3OH}/k_{CH_3OD} is greater than two at 0.05 M but close to unity below 10^{-3} M methanol. Serious experimental errors in papers by Hughes, Ingold, Mok, Patai and Pocker are noted and it is shown that the mechanisms proposed by these authors are unsound.

In 1955, Kreevoy[2] demonstrated that ionization of triphenylmethyl (trityl) chloride can occur in benzene solution assisted by only the solvent. The evidence was his observation that halide exchange occurs at the same rate (zero order in salt) with either a radiochloride or a fluoride quaternary ammonium salt. He also showed that the two salts compete for a common carbonium chloride intermediate when both are present, by the fact that the rate of radiochloride exchange is markedly reduced by the presence of the fluoride salt even before much trityl chloride has been converted to trityl fluoride.

The exchanges with radiochloride were studied down to 0.0006 M concentration of chloride salt. The purpose of the present work was to make a similar study of methanolysis down to very low concentrations, since our earlier work on methanolysis[4] covered the range only from 0.1 to 0.05 M methanol.

For accurate results, the analytical method chosen for studying reactions of 0.1 M trityl chloride with reagents less concentrated than 0.01 M should be based not on trityl chloride, the concentration of which remains relatively constant, but instead on the reagent. For methanolysis we accomplished this by use of methanol labeled with tritium in the methyl group. Methanol remaining was separated from trityl chloride, trityl methyl ether and triphenylmethanol by extraction of aliquots with water, and measured by scintillation counting in water solution. A typical kinetic run in benzene solution containing pyridine at 25° is shown in Fig. 1. Table I (runs 132 and 133) shows that deliberate initial addition of water (1.12×10^{-3} M) at 54 times the initial concentration of methanol (2.06×10^{-5} M) does not affect the measured rate constant of methanolysis more than 4% (within experimental error). With a method based on trityl chloride the change would have been at least 5400% because water is more reactive than methanol (*cf.* runs 105 and 22).

Proof that Tertiary Amines Used are not Involved in the Rate-determining Step.—In reactions with hydroxylic reagents it is necessary to add a base to bind the hydrogen chloride produced, otherwise the reverse reaction soon becomes important and reaction stops far short of completion. We have used tertiary amines for this purpose. We showed earlier[4] that the rate of methanolysis is practically independent of the nature or concentration of tertiary amines used at high concentrations of methanol. Table I shows that the same is true at low concentrations of methanol. The amines used included pyridine, 2,6-lutidine, triethylamine and tribenzylamine (*cf.* runs 120, 121, 123, 128). They cover a wide range in both basicity and steric requirements.[5] That no substantial

Table I

Effect of Water and Amines Used

Run	$(C_6H_5)_3$-CCl, M	CH_3OH, $M \times 10^5$	Water, $M \times 10^4$	Amine, M	$k_2 \times 10^5$,[e] M^{-1} sec.$^{-1}$
132	0.113	0.206	..	0.112[a]	7.92 ± 0.28
133	.114	0.206	11.2	.112[a]	8.22 ± .08
134	.113	2.04	11.1	.112[a]	7.94 ± .16
127	.091	5.55	0.224	.105[a]	6.64 ± .17
126	.088	5.45	2.20	.103[a]	7.56 ± .28
121	.094	5.56	..	.111[b]	5.47 ± .39
123	.095	5.56	..	.087[c]	5.69 ± .33
128	.075	5.51	..	.108[d]	8.53 ± .25
122	.095	5.80	..	.0082[a]	7.89 ± .33
125	.094	5.56	..	.020[a]	6.86 ± .28
124	.095	5.56	..	.080[a]	7.19 ± .28
120	.095	5.45	..	.106[a]	6.72 ± .11
105	.101	442	..	.098[a]	18.2[f]
22	.104	..	101	.100[a]	200[f,g]

[a] Pyridine. [b] 2,6-Lutidine. [c] Triethylamine. [d] Tribenzylamine. [e] Second-order rate constant (first-order in both trityl chloride and methanol) for methanolysis in benzene solution at 25°, calculated from rate of disappearance of methanol determined by scintillation counting of methanol remaining. [f] Calculated from initial rate. [g] Kinetic order appears to be slightly higher than third, with initial k_3 = 0.03 M^{-2} sec.$^{-1}$ Analysis by trityl chloride remaining[4] rather than by scintillation counting for run 22 only.

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(2) For preceding paper on trityl chloride in benzene, *cf.* C. G. Swain and M. M. Kreevoy, This Journal, **77**, 1122 (1955).

(3) For complete details, *cf.* E. E. Pegues, Ph.D. Thesis in Organic Chemistry, M.I.T., August, 1957.

(4) C. G. Swain, This Journal, **70**, 1119 (1948).

(5) The pK_A values of the conjugate acids in water at 25° are 5.23 for pyridine, 6.62 for 2,6-lutidine, 10.78 for triethylamine and <5.6 for tribenzylamine from measurements by A. Gero and J. J. Markham, *J. Org. Chem.*, **16**, 1835 (1951); A. Hantzsch and F. Sebaldt, *Z.*

fraction of the trityl chloride (*i.e.*, no more than a few per cent.) is ever present as tritylpyridinium chloride was shown by the correspondence of the infrared spectrum of a benzene solution of 0.4 *M* trityl chloride and 0.4 *M* pyridine with that for separate solutions of the two reactants in benzene or other solvents, by the absence of any change in the spectrum of this mixed solution from 10 minutes to 47 hours, and by quantitative recovery of trityl chloride by evaporation at 25° of a benzene solution 0.5 *M* in trityl chloride and 0.5 *M* in pyridine after 24 hours (see Experimental section). If formation of tritylpyridinium chloride were involved either in the rate-determining step or in a prior equilibrium step giving it in low concentration as an unstable intermediate, the rate should depend on the concentration of pyridine. Actually the rate increases not at all on increasing the pyridine concentration 13-fold (*cf.* runs 122-120). If anything, there is a slight (15%) decrease. The very minor rate depressions observed at the highest pyridine concentrations or with the stronger amine, triethylamine, probably are due to some complexing with the methanol by hydrogen bonding, which slightly reduces the reactivity of the methanol.[6]

To leave out the tertiary amine would be to invite disaster. Not only would this open the Pandora's box of troubles associated with initial rate measurements on reversible reactions proceding to a small extent in the desired direction, but it would result in powerful catalysis of all reactions by hydrogen chloride initially present, and autocatalysis by hydrogen chloride produced.[7] The use of tertiary amines is a safeguard against such catalysis.

Kinetic Orders in Methanol from 10^{-6} to 10^{-1} *M* Methanol.—Table II shows that the reaction is exactly first order in methanol (second order overall) from initial concentrations of 2×10^{-6} *M* to 4×10^{-3} *M* (*cf.* runs 131-114). The rate constant is essentially constant (mean is 7.5×10^{-5} M^{-1} sec.$^{-1}$). Since kinetic points as late as 74% reaction were still on the best straight line at 2×10^{-6} *M* initial concentration, the known range of constant kinetic order extends from 5×10^{-7} *M* to 4×10^{-3} *M*, *i.e.*, over a range of more than three powers of ten in concentration of methanol.

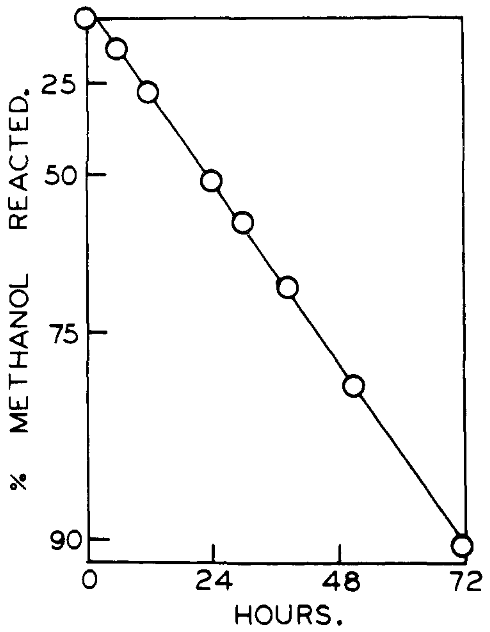

Fig. 1.—Kinetic data for reaction of 2.06×10^{-5} *M* methanol with 0.1141 *M* trityl chloride in benzene solution containing 1.12×10^{-3} *M* water and 0.1120 *M* pyridine at 25°, run 133.

The simplest interpretation of kinetics first order in trityl chloride and first order in methanol over this very considerable range involves rate-determining reaction of triphenylcarbonium chloride with methanol. The rates at low concentrations of methanol are very much less than the rate of ionization of trityl chloride assisted by only benzene as determined by extrapolation from 68°, 50° and 36° to 25° of Kreevoy's rate constants for chloride and fluoride. Since the more nucleophilic reagents, chloride and fluoride (M^+X^-), react only with ionic carbonium chloride (R^+Cl^-) and not with covalent trityl chloride (RCl) at low concentrations, it is likely that the less nucleophilic methanol also reacts only with carbonium chloride rather than performing a direct Walden inversion on covalent trityl chloride at these low concentrations. Rate-determining steps are indicated by asterisks.

TABLE II

EFFECT OF CONCENTRATION OF METHANOL

Run	$(C_6H_5)_3CCl$, *M*	C_6H_5N, *M*	CH_3OH, $M \times 10^4$	$k_2 \times 10^5$,[a] M^{-1} sec.$^{-1}$
131	0.089	0.111	0.0204	8.94 ± 0.61
130	.091	.111	.204	7.89 ± .31
132	.113	.112	.206	7.92 ± .28
104	.101	.098	4.42	6.93 ± .26
102	.101	.098	4.42	7.06 ± .26
120	.095	.106	5.45	6.72 ± .11
110	.105	.100	35.3	7.59 ± .18
107	.101	.100	35.3	7.03 ± .01
114	.102	.100	35.3	7.08 ± .14
108	.101	.100	442	19.6[b]
105	.101	.098	442	18.2[b]

[a] Second-order rate constant (first order in both trityl chloride and methanol) for methanolysis in benzene solution at 25°. [b] Calculated from initial rate.

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physik. Chem., **30**, 298 (1899); and H. Goldschmidt and R. M. Salcher, *ibid.*, **29**, 89 (1899). The basicity (K_B) of triethylamine is 1.8×10^5 times that of tribenzylamine as determined from studies of association with bromophthalein magenta E in benzene at 25° by M. M. Davis and H. B. Hetzer, THIS JOURNAL, **76**, 4247 (1954). In nucleophilic displacements on phosphorus which pyridine and even 2,6-lutidine effect readily, tribenzylamine is too sterically hindered to react according to F. H. Westheimer, personal communication and *Chem. Soc. (London), Spec. Publ.*, No. 6, in press. Thus if the amine functioned as either a base or a nucleophile, the rate with at least one of the other amines should have been many powers of ten faster than that with tribenzylamine, instead of the same or slightly slower as observed.

(6) Both triethylamine and 2,6-lutidine, which give rate constants 15–20% lower than pyridine, are known to associate more strongly than pyridine with methanol-*d* from comparison of shifts in OD stretching frequency by M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3984 (1954).

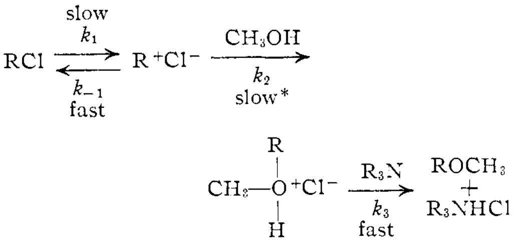
(7) Hydrogen chloride was shown to be a powerful catalyst for alkylations by trityl chloride by H. Hart and F. A. Cassis, *ibid.*, **76**, 1634 (1954). Quaternary ammonium bichlorides have been isolated by H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *ibid.*, **76**, 4046 (1954).

Table III

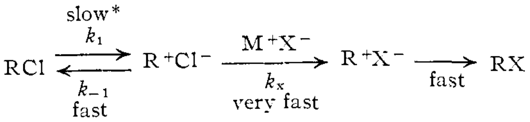
Isotope Effect of Methanol *vs.* Methanol-*d*

Run	$(C_6H_5)_3CCl$, *M*	C_6H_5N, *M*	CH_3OH + CH_3OD,[a] *M* × 10^4	CH_3OD, %	$k_2 \times 10^5$,[b] M^{-1} sec.$^{-1}$	k_H/k_D[d]
114	0.102	0.100	35.3	0.0	7.08 ± 0.14	....
109	.105	.100	37.4	63.6	7.36 ± .17	....
115	.102	.100	30.9	97	6.64 ± .10	1.07 ± 0.03
105	.101	.098	442	0.0	18.2[c]	....
113	.086	.106	601	59.3	11.7 ± .2	....
112	.149	.141	569	60.1	10.3 ± .4	....
118	.102	.100	464	97	8.6 ± .3	>2

[a] Total methanol + methanol-*d*. [b] Second-order rate constant (first order in both trityl chloride and methanol) in benzene at 25°. [c] Calculated from initial rate. [d] Isotope effect, k_{CH_3OH}/k_{CH_3OD}.



$$RCl \underset{k_{-1}\ \text{fast}}{\overset{\text{slow}\ k_1}{\rightleftarrows}} R^+Cl^- \xrightarrow[k_2\ \text{slow*}]{CH_3OH} CH_3{-}\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{O}}{}^+Cl^- \xrightarrow[k_3\ \text{fast}]{R_3N} \begin{matrix} ROCH_3 \\ + \\ R_3NHCl \end{matrix} \qquad (1a)$$



$$RCl \underset{k_{-1}\ \text{fast}}{\overset{\text{slow*}\ k_1}{\rightleftarrows}} R^+Cl^- \xrightarrow[k_x\ \text{very fast}]{M^+X^-} R^+X^- \xrightarrow[\text{fast}]{} RX \qquad (1b)$$

$$\frac{-d(CH_3OH)}{dt} = \frac{k_1k_2(RCl)(CH_3OH)}{k_{-1} + k_2(CH_3OH)} \cong \frac{k_1k_2(RCl)(CH_3OH)}{k_{-1}}$$

$$\frac{-d(M^+X^-)}{dt} = \frac{k_1k_x(RCl)(M^+X^-)}{k_{-1} + k_x(M^+X^-)} \cong k_1(RCl)$$

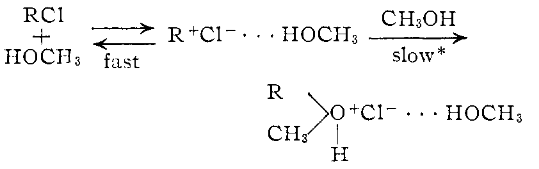
$k_1 \cong 10^{-5}$ sec.$^{-1}$ at 25°; $k_1 << k_{-1}$

$k_2\ (CH_3OH) < k_{-1}$ below 0.004 *M* methanol

$k_{Cl}\ (M^+Cl^-) > k_{-1}$ from 0.0006 to 0.007 *M* chloride

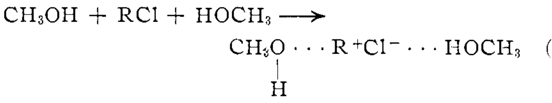
The difference between second-order kinetics over-all with methanol and first-order kinetics with chloride or fluoride is thus determined simply by the fact that the k_2 step with methanol is slower than the k_{-1} step, while the corresponding k_x step with chloride or fluoride is faster than the k_{-1} step. Benzene is not shown explicitly in this mechanism, but is probably involved in solvating, at least electrostatically, both the triphenylcarbonium ion and the chloride ion forming in the first step.

At higher concentrations of methanol, the mechanism is very much less certain. Above 4 × 10^{-3} methanol the total kinetic order increases smoothly and continuously from two to higher than three (order with respect to methanol from one to higher than two) as methanol is increased to 0.1 *M*. The minimum modification of the mechanism operating at low concentrations of methanol (1a) which will accommodate the extra methanol involved at 0.05 *M* methanol is



$$\begin{matrix} RCl \\ + \\ HOCH_3 \end{matrix} \underset{\text{fast}}{\rightleftarrows} R^+Cl^- \cdots HOCH_3 \xrightarrow[\text{slow*}]{CH_3OH} \begin{matrix} R \\ CH_3 \end{matrix}\!\!>\!\underset{\underset{H}{|}}{O}{}^+Cl^- \cdots HOCH_3 \qquad (2)$$

with subsequent steps fast. Here one (or, at higher concentrations, more than one) methanol molecule replaces benzene in electrophilically solvating the chloride ion forming in the first step. The second step is the same as in mechanism 1a. A mixture of phenol and methanol gives a faster rate than either one alone[4] because phenol is still more effective as an electrophile in the first step, while methanol continues to be the most effective nucleophile in the second step. Another mechanistic possibility for the reaction at 0.05 *M* methanol is the one originally proposed[4]



$$CH_3OH + RCl + HOCH_3 \longrightarrow \underset{\underset{H}{|}}{CH_3O} \cdots R^+Cl^- \cdots HOCH_3 \qquad (3)$$

with subsequent steps fast.[8]

Relative Rates with Methanol and Methanol-*d*.—Table III shows that the isotope effect k_H/k_D at low concentrations of methanol is small, *viz.*, 1.07 (runs 114 and 115). Runs 105, 113, 112 and 118 show that it is much larger at high concentrations of methanol. Not only is the rate reduced to one-half with 97% methanol-*d* instead of methanol, but the kinetics appears to be close to second order instead of third order, with a rate constant only slightly higher than that at low concentrations of methanol-*d*. Hydrogen isotopes have been reviewed recently[10a] and the special difficulties in interpreting secondary isotope effects have also been discussed.[10b] In our present system, methanol and methanol-*d* differ only slightly in nucleophilic reactivity (step 2 of mechanism 1a) but considerably more in electrophilic reactivity (step 1 of mechanism 2).

(8) The most unambiguous way to describe a mechanism is to write down all intermediates intended and indicate the rate-determining step, since labels like SN1 and SN2 may mean different things to different people or to the same people at different times. Thus although there would be no controversy in classifying mechanism 1b as SN1, mechanism 1a could be called either SN1 (because it has the same triphenylcarbonium chloride intermediate and same kinds of steps as 1b) or SN2 (because it is second order with a nucleophilic reagent forming a covalent bond in the rate-determining step). Moreover we are no longer satisfied with over-all labels like "medium effect," "co-solvent effect," "push-pull," "termolecular" and "concerted," because as defined they do not differentiate between mechanisms like 2 and 3, which we now believe to be potentially physically distinguishable, although in this instance they are not yet distinguished in practice. With the much more detailed description of polar displacement reactions now emerging from work in many laboratories, rough classifications that formerly were useful have become outgrown.[9]

(9) "First Epistle of Paul to the Corinthians," Chap. 13, 9–13 (58 A.D.).

(10) (a) V. Gold and D. P. N. Satchell, *Quart. Revs.*, **9**, 51 (1955); K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955); (b) S. I. Miller and W. G. Lee, Abstracts of Papers, 130th A.C.S. Meeting, Sept. 16–21, 1956, p. 26 R.

Experimental Errors in the Ingold Papers.—After the work described above was essentially complete, 78 pages of data and discussion by Hughes, Ingold, Mok, Patai and Pocker appeared,[11-17] which contain criticism of work by Swain and Kreevoy, but are very misleading because these authors fail to point out the considerable area of agreement with our previous work,[2] because they made quite serious experimental errors, and because their mechanisms are theoretically unsound.

They studied the reactions of trityl chloride with tetra-*n*-butylammonium radiochloride and azide, methanol, and benzyl alcohol, and conclude that all of these reactions become zero order in the reagent at low enough concentration of the reagent, with ionization of trityl chloride as a universal first step. This is a reversal of their previous view[18] on our methanolysis.[4] They contribute significant new studies of the conductance of various tetra-*n*-butylammonium salts in benzene separately and in mixtures, and with added hydrogen chloride, methanol or phenol.[11] Their zero-order dependence of rate on tetra-*n*-butylammonium chloride concentration from 0.001–0.004 M salt at 25° is in agreement with Kreevoy's work[2] using dimethyldioctadecylammonium chloride; evidently it is not of great importance which quaternary salts are used. Their inhibition of chloride exchange with azide is the exact analog of our earlier inhibition with fluoride,[2] and interpreted in the same way. They found phenol to be a hundred times better catalyst for anion exchanges than nitrobenzene, supporting our conclusion that phenol plays a *specific* role, although they interpret the effect of phenol as a medium or "co-solvent" effect. The more than tenfold greater effect of 0.04 M methanol than of 0.04 M nitrobenzene or nitromethane also points to specific involvement of the methanol. In general their rates at high reagent concentrations, where the effect of adventitious water is relatively small, are in good agreement with ours. Here they also found rates of high and variable order with respect to the reagent.

The largest experimental conflict with our work concerns the kinetic order for methanolysis at low concentrations of methanol. They claim that the kinetic order in methanol drops continuously to zero order as the concentration of methanol drops to 0.002 M. The evidence consists of 26 runs from 0.500 to 0.002 M methanol. The plotted data[14] fall on a smooth curve with very little scatter, indicating good precision and reproducibility (±10%). The rate appears to be independent of methanol concentration (zero order in methanol) from 0.01 to 0.002 M based on at least five runs in this region. Yet our results already described show that the kinetic order is never less than first order in methanol even down to 0.0000005 M. It is first order in methanol at 0.001–0.004 M. The discrepancy appears to be due in part to contaminating traces of moisture, which would invalidate their analytical method, which was based on acid produced and did not distinguish between methanolysis and hydrolysis, but not ours, which was specific for methanol. The difficulty is aggravated by their failure to utilize a tertiary amine to bind the hydrogen chloride produced. This results in catalysis of both methanolysis and hydrolysis by hydrogen chloride. There was always acid present at the start of their runs, sometimes as much as 5×10^{-4} M. Rate constants were calculated from initial slopes over usually less than 1% reaction of the methanol because reaction is reversible in the absence of amine. They omitted the tertiary amine because they claimed that a substantial fraction of it reacts to form quaternary ammonium chloride as an intermediate, which we have shown to be incorrect. The magnitude of their error is a factor of $0.35 \times 10^{-5}/0.002(7.5 \times 10^{-5}) = 23$ in rate at 0.002 M methanol. Although their random errors are only ±10%, this measurement is too high by 2300% because of systematic errors from accidental impurities (water and hydrogen chloride) catalyzing methanolysis and hydrolysis. This inaccuracy is enough to cause them to deduce the wrong kinetic order as well as the wrong rates at their lowest concentrations of methanol.

The rate constants which they report for the rates of exchange with 0.001-0.004 M tetra-*n*-butylammonium azide or chloride may be unreliable because the rates with methanol in that same concentration range were so completely incorrect. Their analytical method for azide was based on trityl chloride, present initially in these runs at 5- to 20-fold higher concentration than the azide. The water and acid evidently present in their methanolysis reactions was probably also present in their azide exchanges, and might catalyze the exchange with azide even more than the methanolysis, because they found that phenol catalyzed azide exchange more strongly than methanolysis. On the other hand, hydrolysis by adventitious water might make the measured rate of exchange with radiochloride relatively lower by diluting the radiochloride with ordinary chloride ion and so retarding the appearance of radiochloride in the trityl chloride, where it was measured. Therefore we doubt that their rate constants have the experimental accuracy needed to justify their conclusion that the zero-order exchange with azide is five times faster than the zero-order exchange with chloride. We did not attempt studies with azide below 0.014 M (where the rate still depends on azide concentration[2]), because we did not see a convenient specific analytical method capable of giving accurate rates of azide exchange at lower concentrations. Our

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(11) E. D. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).

(12) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *ibid.*, 1220 (1957).

(13) E. D. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *ibid.*, 1230 (1957).

(14) E. D. Hughes, C. K. Ingold, S. F. Mok and Y. Pocker, *ibid.*, 1238 (1957).

(15) E. D. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *ibid.*, 1256 (1957).

(16) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *ibid.*, 1265 (1957).

(17) Y. Pocker, *ibid.*, 1279 (1957).

(18) "The much more probable interpretation (E. D. Hughes, personal communication) is that such a substitution, in the completely non-ionizing solvent, benzene, is an S_N2 reaction, $MeOH + Ph_3CCl \rightarrow Ph_3COMe + HCl$" (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 356).

mechanism 1b predicts that azide exchange should be first order in trityl chloride and zero order in salt around 0.001 *M*, with a rate constant then equal to that for chloride or fluoride exchange, but should change back to second order at still lower concentrations when the rate of the k_X step becomes slow relative to the k_{-1} step as in mechanism 1a.

Inconsistencies in the Ingold Mechanisms.—They are convinced (we believe without proper evidence because of experimental errors already cited) that the rate of exchange is independent of the concentration of reagent in the neighborhood of 0.001 *M*, yet still depends on the nature of the reagent. To explain this they proposed mechanisms which are theoretically unsound. Their first suggestions, which include mechanism 4

$$\begin{tikzcd} \mathrm{RCl} \arrow[r, "\text{slow}"] & \mathrm{R^+Cl^-} \arrow[r, "\text{fast}"] & \mathrm{X^-R^+Cl^-} \arrow[r, "\text{fast}"] \arrow[d, "\text{fast}"] & \mathrm{RCl} \quad (4) \\ & & \mathrm{RX} & \end{tikzcd}$$

violate the principle of microscopic reversibility[19] because they involve irreversible routes from RCl to RCl. However, their final scheme suffers from serious difficulties of a more subtle kind.

$$\mathrm{RCl} \underset{\substack{k_{-1}\\ \text{fast}}}{\overset{\substack{\text{slow}\\ k_1}}{\rightleftarrows}} \mathrm{R^+Cl^-} \underset{\substack{k_{-2}\\ \text{fast}}}{\overset{\substack{\mathrm{M^+X^-}\\ \text{fast}\\ k_2}}{\rightleftarrows}} \begin{bmatrix}\mathrm{R^+Cl^-}\\ \mathrm{M^+X^-}\end{bmatrix} \underset{\substack{k_{-3}\\ \text{slow}}}{\overset{\substack{\text{slow}\\ k_3}}{\rightleftarrows}}$$

$$\begin{bmatrix}\mathrm{R^+X^-}\\ \mathrm{M^+Cl^-}\end{bmatrix} \underset{\substack{k_{-4}\\ \text{fast}\\ \mathrm{M^+Cl^-}}}{\overset{\substack{\text{fast}\\ k_4}}{\rightleftarrows}} \mathrm{R^+X^-} \underset{\substack{k_{-5}\\ \text{slow}}}{\overset{\substack{\text{fast}\\ k_5}}{\rightleftarrows}} \mathrm{RX} \quad (5)$$

Although they do not derive a rate expression from it, one can be obtained by using the steady-state assumption for all intermediates.

$$\text{rate} = \frac{k_1k_2k_3k_4k_5(\mathrm{RCl})(\mathrm{M^+X^-}) - k_{-1}k_{-2}k_{-3}k_{-4}k_{-5}(\mathrm{RX})(\mathrm{M^+Cl^-})}{k_2k_3k_4k_5(\mathrm{M^+X^-}) + k_{-1}k_3k_4k_5 + k_{-1}k_{-2}k_4k_5 + k_{-1}k_{-2}k_{-3}k_5 + k_{-1}k_{-2}k_{-3}k_{-4}(\mathrm{M^+Cl^-})}$$

If k_1, k_3, k_{-3} and k_{-5} are small and all other rate constants large, as they indicate, the initial rate should be

$$\text{rate} = \frac{k_1k_2k_3k_4k_5(\mathrm{RCl})(\mathrm{M^+X^-})}{k_2k_3k_4k_5(\mathrm{M^+X^-}) + k_{-1}k_{-2}k_4k_5 + k_{-1}k_{-2}k_{-3}k_{-4}(\mathrm{M^+Cl^-})}$$

If the first term in the denominator is large compared to the other two so that the rate becomes independent of the concentration of $\mathrm{M^+X^-}$, the rate should also become independent of the nature of $\mathrm{M^+X^-}$. If the middle term in the denominator dominates, the experimentally observed independence of rate on the concentration of $\mathrm{M^+X^-}$ is not predicted. The mechanism appears to be incompatible with what it was designed to explain.

In the special case of radiochloride exchange, $k_3 = k_{-3}$, $k_4 = k_{-2}$, $k_{-4} = k_2$, $k_5 = k_{-1}$ and $k_{-5} = k_1$ to a good approximation, yielding

$$\text{rate} = \frac{k_1k_2k_3(\mathrm{RCl})(\mathrm{M^+Cl^-})}{2k_{-1}k_3 + k_{-1}k_{-2} + k_2k_3(\mathrm{M^+Cl^-})}$$

The same difficulty is apparent. The zero-order dependence on salt requires the last term in the denominator to dominate. But then the rate reduces to $k_1(\mathrm{RCl})$, which is simply the rate of the first step, which should not depend on the nature of the salt.

Let us suppose again that the middle term in the denominator dominates in all these equations

$$\text{rate} = \frac{k_1k_2k_3(\mathrm{RCl})(\mathrm{M^+X^-})\gamma_{\mathrm{RCl}}\gamma_{\mathrm{M^+X^-}}}{k_{-1}k_{-2}\gamma^*}$$

Activity coefficients (γ) for RCl, $\mathrm{M^+X^-}$ and the transition state have now been added to allow for variable electrostatic salt effects. Could this rate law be compatible with an experimental zero-order dependence on $\mathrm{M^+X^-}$ because changes in one or more of these activity coefficients exactly offset changes in concentration of $\mathrm{M^+X^-}$? We believe not for the following reasons. Compensation by a rapidly falling activity coefficient for $\mathrm{M^+X^-}$ would be possible only if these quaternary salts formed micelles or very large aggregates in the 0.001–0.01 *M* range in question. In fact they are small aggregates, mostly dipoles and quadrupoles.[11,20] Freezing-point depressions of tetra-*n*-butylammonium salts in benzene vary more than fivefold over the concentration range 0.001–0.01 *M*, or over any tenfold range below 0.01 *M*, showing that aggregation number changes only very slowly with concentration.[20] Therefore the activity of $\mathrm{M^+X^-}$ does not remain constant because of offsetting changes in its stoichiometric activity coefficient. The activity coefficient of RCl is likely to be affected still less because it is uncharged. It is irrelevant to consider $\mathrm{R^+Cl^-}$, which is an intermediate; only the normal ground state of the reactants in solution (RCl and $\mathrm{M^+X^-}$) and the transition state affect the rate. The only variable left is the activity coefficient of the transition state. If it were to rise approximately proportionally to the concentration of $\mathrm{M^+X^-}$ (with its activity proportional to the square of the concentration of $\mathrm{M^+X^-}$), this would give zero-order kinetics. However, it seems quite unreasonable that $\mathrm{M^+X^-}$ should so increase the activity coefficient of the transition state when it produces a relatively small effect on its own activity coefficient (and in fact lowers it rather than raises it). In short we should not expect $\mathrm{M^+X^-}$ to stabilize covalent RCl relative to the polar transition state by a factor proportional to the concentration of $\mathrm{M^+X^-}$. We should expect it to have either no effect or else the opposite effect of stabilizing the polar transition state relative to covalent RCl. Thus a first-order rate law with variable activity coefficients also fails to predict the observed independence of rate on concentration of $\mathrm{M^+X^-}$.

To predict the observed independence of rate on the concentration of $\mathrm{M^+X^-}$, it is not sufficient to have one $\mathrm{M^+X^-}$ "ubiquitously present in the transition states"[16] unless one $\mathrm{M^+X^-}$ is also ubiquitously

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[19] P. D. Bartlett in H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1953, p. 9; A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 202.

[20] D. T. Copenhafer and C. A. Kraus, THIS JOURNAL, **73**, 4559 (1951); D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

associated with RCl in the ground state. The latter could not be true unless Cl were mostly ionized in the ground state, which its visible absorption spectrum shows it not to be.

On the other hand, it would be possible to interpret the results by a quite different kind of mechanism if exchange with 0.001 *M* azide ion really were five times faster than exchange with 0.001 *M* radiochloride, with each reaction zero order in salt. This behavior would be consistent with a mechanism involving two successive intermediates, with azide able to exchange with either II or III, but chloride or fluoride able to exchange with only III.

$$\mathrm{RCl}\ \underset{\substack{k_{-1}\\ \text{fast}}}{\overset{\substack{\text{slow}\\ k_1}}{\rightleftharpoons}}\ \mathrm{II}\ \underset{\text{fast}}{\overset{\substack{\text{very}\\ \text{slow}\\ k_2}}{\rightleftharpoons}}\ \mathrm{III}\ \underset{\substack{\mathrm{M^+Cl^-}\\ \text{very}\\ \text{fast}}}{\overset{\substack{\mathrm{M^+Cl'^-}\\ \text{very}\\ \text{fast}}}{\rightleftharpoons}}$$

$$\mathrm{III'}\ \underset{\substack{\text{very}\\ \text{slow}}}{\overset{\text{fast}}{\rightleftharpoons}}\ \mathrm{II'}\ \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}}\ \mathrm{RCl'} \qquad (6)$$

$$\text{II or III}\ \underset{\substack{\text{very}\\ \text{slow}}}{\overset{\substack{\mathrm{M^+N_3^-}\\ \text{very}\\ \text{fast}}}{\rightleftharpoons}}\ \mathrm{RN_3}$$

If radiochloride, chloride, or azide were involved in only steps with very large rate constants, the over-all rate would be independent of their concentrations. The rate expression derived by applying the steady-state assumption to all intermediates in mechanism 6 is

$$\text{rate} = k_1(\mathrm{RCl})$$

for azide exchange and

$$\text{rate} = \frac{k_1 k_2(\mathrm{RCl})}{k_{-1} + k_2}$$

for chloride or fluoride exchange. These rates may be different if $k_{-1} > k_2$. The essential difference between mechanisms 5 and 6 is that in 5 M^+X^- is present in the transition state, whereas in 6 it is not present in the transition state but enters only in a subsequent fast step. Mechanism 6 is obtained by expanding mechanism 1b to include two kinds of carbonium chloride ion pairs (II and III) rather than one (R^+Cl^-). The intermediate II might be a simple triphenylcarbonium chloride ion pair or a π-complex with benzene or a σ-complex (covalent addition product) with benzene, and III might be a different one of these three species. Mechanisms with two or more kinds of ion pairs were proposed some time ago by Winstein and co-workers for reactions in acetic acid,[21] and are quite reasonable for the systems which Winstein and co-workers studied. However, for reasons given in the previous section, it will be necessary to do further experiments to decide if there is evidence for such multiplicity of intermediates in the case of trityl chloride in benzene.

It is also possible to have a mass effect of chloride ion (induced common-ion rate depression) in solvents of low dielectric constant when salts with other anions are present, as found by Winstein,[21] but the simplest *tenable* interpretation involves reversible exchange between ion aggregates as proposed by Winstein.[21]

Experimental

Benzene.—Analytical reagent benzene was dried by distilling approximately 10% to remove the water–benzene azeotrope and storing the remainder over sodium wire.

Trityl Chloride.—Two methods of preparation were used giving material of the same m.p. 111–112°, and apparently the same purity as judged from kinetics: (1) Matheson research grade or Eastman Kodak Co. white label chemical was once or twice recrystallized from benzene–petroleum ether mixture; (2) triphenylmethanol prepared by a Grignard procedure was purified by steam distillation, recrystallized from ethanol and converted to trityl chloride by the method given by Bachmann.[22] For runs 132–134, trityl chloride was purified further by slow sublimation at 130° under 2 mm. pressure, to ensure the absence of acetyl chloride. Large colorless crystals were obtained.

Methanol.—Reagent grade methanol was dried over Drierite.[23]

Methanol-*d*.—The procedure for the preparation of methanol-*d* was that of Redlich and Pordes.[24] It involved decomposition of magnesium methylate with deuterium oxide. Five grams of magnesium was treated with 90 ml. of methanol and, after disappearance of the magnesium, the methanol removed by distillation. The dry residue was heated at 220° under 35 mm. pressure for one hour; 6 ml. of deuterium oxide (>99.5 % from Stuart Oxygen Co.) was added with no apparent change in the powdery solid. When this solid material was heated at atmospheric pressure, 16 ml. of liquid distilled. Magnesium (0.4 g.) was added and the methanol-*d* redistilled through a semi-micro column.[25] The first 5 ml. was discarded and the next 3 ml. used to make up stock solutions in benzene. This material was found by infrared analysis to contain 37% OH calculated as methanol.

Methan-*t*-ol.—The method of Melander[26] was used in the preparation of methanol with tritium substituted on carbon. Diazomethane, prepared from N-nitrosomethylurea,[27] was allowed to react with an ether solution of benzoic acid to which tritiated water with an activity of approximately 3 curies per mole had been added. The methyl benzoate was hydrolyzed with aqueous potassium hydroxide, an equivalent molar amount of reagent methanol added, and the total methanol fractionally distilled. Six fractions boiling between 64 and 65° were collected and sealed in weighed Pyrex ampoules. Each fraction was approximately 0.6 g., an amount calculated to give 100 ml. of a 0.2 *M* stock solution. The activity of this methan-*t*-ol, when compared by liquid scintillation counting with a sample of toluene of known absolute activity, was found to be approximately 60 millicuries per mole. If conversion of tritiated water to methanol had been complete, the calculated activity would have been 440 millicuries per mole. Methanol, prepared by using the same procedure and equipment, was found by Karl Fischer titration to contain 0.09 ± 0.14% water.

A second preparation of methan-*t*-ol using the same procedure was carried out with water having a higher specific activity. This water had been prepared in this Laboratory by Dr. A. J. Kresge using platinum-catalyzed H_2O–T_2 exchange. The methan-*t*-ol so prepared had an activity of approximately 4 curies per mole and was used for ru 130–134.

Methan-*t*-ol-*d*.—Methan-*t*-ol (1.5 ml.), 1.5 ml. of methanol and 6 ml. of deuterium oxide were equilibrated and fractionally distilled through a semi-micro column.[25] A

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[21] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956); **76**, 2597 (1954).

[22] W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943); Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 841.

[23] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 293.

[24] O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936).

[25] C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[26] L. Melander, *Arkiv Kemi*, **3**, 525 (1951).

[27] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 165, 461.

2.8-ml. fraction boiling at 65.9° was collected and equilibrated with 5 ml. of deuterium oxide; from this was distilled 2.6 ml. boiling at 65.8°. Drierite was added and the material left overnight. From this, approximately 1.5 ml. was distilled at 65.2° into a tared test-tube which was sealed and weighed. Methanol-*d* previously prepared using the same procedure and apparatus was found by infrared analysis to contain a maximum of 3% methanol (*vs.* calcd. 2.5% for complete exchange and no isotope fractionation).

Pyridine.—Analytical reagent pyridine was dried several days over Drierite.

2,6-Lutidine.—Approximately 100 g. of Reilly Chemical Co. 2,6-lutidine was treated with 14.3 g. of aluminum chloride to complex the picolines preferentially and to remove water.[28] The mixture was distilled through a Podbielniak column with 12 in. of Hastelloy B Heligrid packing (about 20 T.P.). A 15-ml. forerun boiling below 143° was discarded and the next 30-ml. fraction, b.p. 143.8°. stored over Drierite.

Tribenzylamine.—Eastman Kodak Co. white label tribenzylamine was recrystallized from absolute ethanol and dried under vacuum, m.p. 92° (lit.[5] 92.8–93.2°). A saturated solution of this material in benzene was titrated with perchloric acid in acetic acid using methyl violet in bromobenzene as indicator.[29]

Triethylamine.—Eastman Kodak Co. white label chemical was redistilled and dried over Drierite, b.p. 89–90° (lit.[30] 89.5°).

Scintillation Solution.—To 770 ml. of analytical reagent toluene and 230 ml. of absolute ethanol was added 4 g. of Arapahoe Chemicals scintillation grade 2,5-diphenyloxazole and approximately 15 mg. of Matheson research grade diphenylhexatriene.[31,32]

Analysis of Methanol-*d*.—Total OH-content of the methanol-*d* expressed as methanol was determined quantitatively by infrared absorption. A first attempt to obtain an OH band calibration in carbon tetrachloride was unsuccessful because of the appearance of both hydrogen-bonded and non-bonded bands. The non-bonded bands disappeared when dioxane was used as solvent, and a calibration at 3530 cm.$^{-1}$ obeying Beer's law from zero to 0.8% methanol by volume was obtained. The equation for this calibration is $\log (I_0/I) = 0.313C$ where C is % methanol in dioxane (volume as % of final volume). The relative amounts of OH and OD were shown not to affect this calibration.

Infrared Studies on Solutions of Trityl Chloride and Pyridine in Benzene and Recovery of Trityl Chloride from these Solutions.[33]—No precipitate was observed in kinetic runs at low methanol concentration, or even in a solution of 0.2 *M* trityl chloride and 0.2 *M* pyridine in benzene after 24 hours at 25°. The infrared spectrum of 0.12 *M* trityl chloride in benzene determined in a Perkin–Elmer model 21 double-beam spectrophotometer with benzene in the reference cell had numerous characteristic peaks including 890 and 1450 cm.$^{-1}$, while that of 0.11 *M* pyridine in benzene also had characteristic peaks including 1440 and 1580 cm.$^{-1}$. The spectrum of a benzene solution containing both 0.12 *M* trityl chloride and 0.11 *M* pyridine which had been standing at room temperature for six hours showed no new bands not present in the separate solutions of trityl chloride or pyridine; it appeared to be a composite of the two. The same was found to be true with 0.42 *M* trityl chloride and 0.42 *M* pyridine in benzene. There was no detectable change in spectrum from 10 minutes after mixing to 47 hours. The same was true in carbon tetrachloride solutions, using 0.11 *M* trityl chloride and 0.13 *M* pyridine, separately and together, and observing for 24 hours.

Trityl chloride was recovered in quantitative yield, m.p. 109–111°, carbon and hydrogen analyses both correct within 0.25%, from a solution of 0.5 *M* trityl chloride and 0.5 *M* pyridine in benzene after 24 hours at 25° by evaporating under vacuum in a rotary evaporator at 25°. It was not necessary to add a higher-boiling solvent to prevent concentrating the pyridine.

Only by addition of water is it possible to obtain a precipitate from trityl chloride and pyridine in benzene or pure pyridine solutions.

Anal. Calcd. for $C_{24}H_{22}NOCl$: C, 76.68; H, 5.90; N, 3.73; Cl, 9.43. Found: C, 76.53; H, 5.90; N, 3.90; Cl, 8.96.

The infrared spectrum of this white solid in a potassium bromide or potassium chloride pellet or in chloroform solution appears to be a composite of the spectra of triphenylcarbinol and pyridine hydrochloride. Crystals with the same melting point, 175–177.5° without decomposition, no depression on mixing, were obtained from a chloroform solution of triphenylcarbinol (m.p. 161–162°) and pyridine hydrochloride (m.p. 82–85°). The solubility of the substance in benzene is less than 0.007 *M*. Since no precipitate forms in kinetic runs with 0.1 *M* trityl chloride, 0.1 *M* pyridine and low concentrations of methanol, no major fraction of the trityl chloride in those runs is ever in this form.

Kinetic Procedure.—Stock solutions were prepared by weight in volumetric flasks and, where possible, were checked by titration. The flasks were sealed with paraffin between runs. All pipets and flasks were dried in an oven at 130° and cooled in desiccators over Drierite before use. A single pyridine stock solution was used with appropriate dilutions for determining the effect of pyridine concentration on rate of methanolysis. A stock solution of water in benzene (0.0364 g. in 100 ml. of solution) was used for run 22. For all other runs using water, a solution was made up by volume from a micropipet; 0.02 ml. of water was added to benzene in a 100-ml. volumetric flask to give 0.011 *M* water. Methan-*t*-ol stock solutions were made by breaking a weighed ampoule under benzene in a volumetric flask; a small correction was made for the volume of glass introduced.

Stock solutions of all reagents used except methanol were mixed in a volumetric flask in proportions calculated to give desired final concentrations. A measured sample, usually 1.0 ml., was added to an excess of methanol and later titrated with standard sodium hydroxide for total trityl chloride. At zero time methan-*t*-ol was added, the solution thoroughly mixed, and placed in a 25° bath. Silicone grease was used on the ground glass stopper, which was held firmly in place by a spring clamp. Immediately and at appropriate subsequent times, an aliquot was pipetted into an accurately measured volume of water contained in a separatory funnel. The relative amounts of water and sample were constant within a run but were adjusted from run to run to give reasonable counting rates. The mixture was shaken vigorously and, after 30 min., when the phases began to separate, it was shaken again. After standing undisturbed for a day, the solutions were clear and a portion of the aqueous phase was withdrawn. Exactly 1.00 ml. of this solution was dissolved in 65 ml. of scintillation solution contained in a counting bottle. These bottles were placed in a refrigerator at −10° where they were counted usually after one run had been completed, using a Tracerlab CE-1 liquid scintillation counter. Background, usually 200 to 250 counts per minute, was determined at least once a day. The sample for zero time was usually counted at intervals between the later samples, so that errors due to instrument drift were minimized. In general, a sample was counted for at least 10,000 counts and, except for the weakest samples, this was repeated until a total of 100,000 counts had been recorded. Percentage reaction was calculated from counts per second at zero time (S_0) and at the sampling time (S_t) as $100\,(S_0 - S_t)/S_0$. For the runs at low concentrations of methanol, first-order rate constants k_1 were calculated by the method of least squares.

$$\Sigma(2.303 \log [a/(a - x)] - k_1t - c)^2 = \text{minimum}$$

where a and x are concentrations of methanol initially and at time t, and were converted to second-order constants by dividing by the trityl chloride concentration. The ± figures reported are standard deviations, which reflect the randomness of points within the runs but do not express estimated systematic errors. The assumption was made that there is no significant error in time because of the long half-life for

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[28] H. C. Brown, S. Johnson and H. Podall, THIS JOURNAL, **76**, 5556 (1954).

[29] L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 159.

[30] A. I. Vogel, *J. Chem. Soc.*, 1832 (1948).

[31] E. C. Farmer and I. A. Berstein, *Science*, **117**, 279 (1953).

[32] C. A. Ziegler, D. J. Chleck and J. Brinkerhoff, *Anal. Chem.*, **29**, 1774 (1957).

[33] We are indebted to Dr. Alexander MacLachlan for making some of the infrared studies and to Dr. Y. Okamoto for recovering trityl chloride from these solutions.

methanol (about 24 hours at low concentrations of methanol).

Tests on Reliability of Extraction Procedure.—Three 10-ml. samples of kinetic solution containing 0.1015 *M* trityl chloride, 0.0984 *M* pyridine and 0.00884 *M* methanol were extracted with 10 ml. of water each. The first was extracted once, the second twice successively, and the third three times. The activities of the remaining organic phases were the same within 1.7%, with the highest activity in the third. This test demonstrates the sufficiency of only one extraction when equal volumes of water and sample are used. Single extractions of this same kinetic solution were made using 15-ml. samples with 10- and 5-ml. volumes of water, respectively. The activity of the aqueous phase of the second was twice that of the first within experimental error (less than 2%).

Methanol, at a concentration higher than any used kinetically, was shown not to increase the solubility of trityl methyl ether in water. Two samples from run 111 which had been left for 16 days and was calculated to contain 0.057 *M* trityl methyl ether were extracted with water alone and with water containing 0.08 *M* methanol. There was no difference in activity between the two aqueous phases: the first gave 15.7 counts per second and the second. 15.3 counts per second. The equivalent initial methanol activity for this run was 3780 counts per second.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Hydrolysis and Deuterium Exchange of Dibromofluoromethane and Fluorodiiodomethane[1]

BY JACK HINE, RICHARD BUTTERWORTH AND PAUL B. LANGFORD

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Rate constants and heats and entropies of activation have been determined for the basic hydrolysis and the deuterium exchange of dibromofluoromethane and fluorodiiodomethane in aqueous solution. The hydrolysis of bromodichloromethane and dibromochloromethane also was studied. For all four haloforms the data support the hydrolysis mechanism in which trihalomethyl anions, formed reversibly from haloform and base, decompose to dihalomethylenes, reactive intermediates that react quickly, either with halide ions to regenerate haloform or with water and alkali to give carbon monoxide or formate ions. The effect of added salts on the rate of the hydrolysis of dibromofluoromethane is compared with their effect on bromodichloromethane and dibromochloromethane in order to learn how variations in the structure of dihalomethylenes affect the efficiency with which the dihalomethylenes may be captured by halide ions. The intermediates, dichloromethylene and bromochloromethylene, are captured with roughly equal efficiency, while bromofluoromethylene is captured with much less efficiency, if at all. While the rate of exchange of deuterodibromofluoromethane was about that expected from data on other haloforms, deuterofluorodiiodomethane exchanged more rapidly than anticipated.

In earlier articles[2] evidence was presented to show that the basic hydrolysis of several haloforms involves the intermediate formation first of a trihalomethyl anion and then a dihalomethylene. In order to investigate the generality of this reaction mechanism for haloforms as well as to learn more about the effect of structure on reactivity in trihalomethyl anion and dihalomethylene formation, we have studied the hydrolysis and deuterium exchange of dibromofluoromethane and fluorodiiodomethane. We also have studied briefly the effect of the structure of dihalomethylenes on their ease of capture by halide ions.

Results and Discussion

Hydrolysis.—Although the fluorodiiodomethane prepared by the reaction of iodoform with mercuric fluoride boiled higher than that reported by Ruff and co-workers[3] or by Haszeldine,[4] the agreement of the boiling point with that predicted from an empirical equation for correlating the boiling points of halomethanes[5] as well as the agreement of the molar refractivity and iodine analysis with the calculated values support the assignment of the $CHFI_2$ structure.

We have studied the hydrolysis of fluorodiiodomethane in aqueous solution at 0 and 20.85°. The rate constants were calculated from the equation used previously[2]

$$k = \frac{2.303}{t(a[3+f] - b)} \log \frac{b(a-x)}{a(b - [3+f]x)} \qquad (1)$$

where $a = [CHX_3]_0$, $b = [OH^-]_0$, $x = a - [CHCl_3]_t$, t = time, f = fraction of haloform that hydrolyzes to formate (the rest gives carbon monoxide), and k is expressed in liters/mole of haloform × seconds. In Table I are listed these data and heats and entropies of activation calculated from the absolute rate equation[6]

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

TABLE I

BASIC HYDROLYSIS OF DIBROMOFLUOROMETHANE AND FLUORODIIODOMETHANE IN AQUEOUS SOLUTION

	$CHBr_2F$	$CHFI_2$
10^3k at 0°	2.77 ± 0.03	0.153 ± 0.003
10^3k at 20.85°	70.8 ± 2.9[a]	6.15 ± .13
$\Delta H^{\ddagger}$, kcal./mole	25.7 ± 0.5	27.7 ± .3
$\Delta S^{\ddagger}$, e.u.	24.1 ± 2.0	25.6 ± 1.2

[a] At 19.6°.

Preliminary tests showed that dibromofluoromethane was the most reactive haloform that we have studied. The rate constants obtained in the first runs at 0° fell considerably as the reaction proceeded. This was found to be due to the temperature of the reaction solution being significantly above 0° for the first few minutes of the reaction.

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[1] Part X in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part IX, see ref. 21. This work was supported in part by the Office of Ordnance Research, U. S. Army.

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[5] J. Hine and S. J Ehrenson, *J Org. Chem.*, **21**, 819 (1956).

[6] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.