[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Thermal Decomposition of Trifluoroacetyl Hypofluorite

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The thermal decomposition of trifluoroacetyl hypofluorite, C_3FCOOF, into CO_2 and CF_4 has been studied at pressures of 1.5 to 3 mm. and temperatures from 30 to 80° in a reactor made of aluminum phosphate glass. The rate of reaction was followed by pressure change. The decomposition proceeds by a chain mechanism with an activation energy of 11.2 kcal., the chains probably being carried by CF_3 radicals. Through the use of chlorine and bromine as free radical traps the initial step has apparently been isolated. This is found to be a second-order reaction with an activation energy of 25 kcal., which is believed to be the energy of the oxygen–fluorine bond in this compound.

Of the seven compounds known to contain an oxygen–fluorine bond, the kinetics of the decomposition of only two, OF_2 and O_2F_2, have been studied. Schumacher[2] reports a 39 kcal. activation energy for the decomposition of OF_2[2] and 17 kcal. for the decomposition of O_2F_2[3] into the elements.

The current article describes the thermal decomposition of trifluoroacetyl hypofluorite (CF_3COOF). Mechanisms are proposed and an estimate of the energy of the oxygen–fluorine bond in this compound is given.

Experimental

Materials.—Fluorine used in this work was obtained from the Pennsylvania Salt Manufacturing Company in half-pound cylinders and was used without further treatment. Trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Company. It was distilled in all-glass apparatus and the portion boiling between 70.6 and 70.9° at 760 mm. was used. The acid appeared to be of high purity, however, and for a number of runs was used as it came from the manufacturer.

Water pumped nitrogen from a steel cylinder was passed through silica gel and Drierite.

Preparation of Trifluoroacetyl Hypofluorite.—This compound was prepared by the method used by Cady and Kellogg.[4] Nitrogen was bubbled at a rate of 8 l./hr. through trifluoroacetic acid in a trap maintained at 0°. The nitrogen and trifluoroacetic acid vapor were then mixed with elemental fluorine in a 250-cc. polyethylene bottle containing 2–3 ml. of water. The fluorine was introduced at 0.8 l./hr. The stream of gas then passed through two polyethylene traps at −78° which removed unreacted acid, water vapor and hydrogen fluoride produced by the reaction. At the start of a preparation run tests were made to show that the apparatus was functioning properly. A sample of product was condensed in a U-tube trap at −183° for a 20-sec. period. The tube was then allowed to warm at room temperature for 1 min.; a copper wire was then inserted and the sparking end of a "leak tester" was touched to the wire. This sampling and sparking procedure was repeated until a sharp explosion caused by the spark within the U-tube indicated a satisfactory rate of production of the compound. Trifluoroacetyl hypofluorite was then collected at −183° in a U-tube which was flattened at the bend. The product was collected for from 45 to 60 minutes. At the end of a preparation run the product was allowed to warm slowly to −78° and stored in a Dry Ice–acetone mixture. At this temperature the compound was a liquid having a vapor pressure of about 30 mm.

Several methods of distillation were attempted and abandoned when they resulted in explosions. The method of purification finally used was to bubble dry nitrogen through the trifluoroacetyl hypofluorite in the U-tube at −78°. The more volatile substances were swept out at first in this manner and the less volatile ones remained behind at the end. After the volatile impurities including SiF_4, CF_4 and CO_2 had been swept away nearly all of the remaining material was trifluoroacetyl hypofluorite. Only a small amount of a material much less volatile than this was also present.

During the first part of the purification process small samples were collected periodically at −183°, pumped to remove nitrogen, and then allowed to evaporate into the line. The vapor was then caused to explode by the spark from a leak tester, and the pressure change was noted on a mercury monometer. Pure trifluoroacetyl hypofluorite vapor exhibited a twofold pressure increase on explosion. When a sample exhibited a doubling of pressure on explosion, the supply of hypofluorite was swept by nitrogen for an additional four minute period at four l./hr. The product was then used for rate studies. The collecting and sampling traps were enclosed in explosion shields made of plywood 19 mm. thick. These proved adequate for the protection of the operator but they were severely damaged at times.

Decomposition Studies.—For a decomposition reaction a sample was collected at −183° for a given time at known nitrogen flow rate. With practice the desired quantity of trifluoroacetyl hypofluorite could be obtained rather accurately in this way. With the sample at −183°, stopcocks to the reactor were opened and the system was evacuated to a pressure of 10^{-3} mm. or lower. The pump was then shut off from the system and the trifluoroacetyl hypofluorite allowed to evaporate. The pressure in the reactor was read on a special manometer. After all of the compound had evaporated the stopcock to the reactor was closed and the rate of decomposition was followed by observing the pressure change. The manometer utilized as a manometer liquid Kel-F fluorocarbon polymer oil #3 manufactured by the M. W. Kellogg Company. This oil had a density of 1.92 g./ml., a low vapor pressure and was inert to trifluoroacetyl hypofluorite. A float valve retained the oil in the manometer when an explosion shattered the sample tube and admitted atmospheric pressure to the reactor.

The reactor was enclosed in an air thermostat, the temperature of which could be controlled to ±0.5°. Temperatures were read with two copper–constantan thermocouples taped to the reactor on opposite sides and covered with asbestos paper.

Analyses.—The products of the decomposition were analyzed by mass spectrometer and chemical analysis. For chemical analyses the products from a considerable number of runs were combined and reacted with standard base. The molecular weights of the portions that did and did not react were determined by vapor density measurements and the acid equivalent weight of the portion absorbed in the base was determined by titration. The products were primarily carbon dioxide and carbon tetrafluoride. Some carbonyl fluoride was present together with a trace of hexafluoroethane. Mass spectrograph records showed peaks at mass numbers 150 and 169, possibly from C_3F_8. A small amount of silicon tetrafluoride was also indicated by the mass spectrum.

Discussion

Decomposition in Copper Reactor.—A number of runs were made in a copper reactor of about 600-ml. capacity with a well fluorinated surface. In the absence of an inhibitor the decomposition was extremely rapid in this vessel at room temperature, reaching completion in about two minutes. With

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[1] This paper is based upon the Ph.D. thesis of R. D. Stewart, University of Washington, 1954.

[2] H. J. Schumacher, "Chemisches Gasreaktionen," T. Steinkopf, 1938, p. 122.

[3] H. J. Schumacher, ref. 2, p. 124.

[4] G. H. Cady and K. B. Kellogg, THIS JOURNAL, **75**, 2501 (1953).

an excess of oxygen present as inhibitor, the decomposition was first order, the pressure doubling.

The reaction occurred in part at the surface as was shown by a tenfold increase in rate when the reactor was cleaned with dilute nitric acid. The activation energy of the inhibited decomposition was estimated from runs at two temperatures to be 7 kcal. in the vessel with a clean surface.

Non-inhibited Decomposition in Phosphate Glass Reactor.—This reactor was made of an aluminum phosphate glass composed of about 75% P_2O_5 with the remainder consisting of Al_2O_3, ZnO, MgO, B_2O_3, CaO, Na_2O, F and less than 0.5% SiO_2. The glass was manufactured by the Haverford Glass Co., Haverford, Pa. Previous work in a Pyrex glass reactor indicated that trifluoroacetyl hypofluorite slowly attacked the wall and caused poor reproducibility, especially at temperatures above 45°.

For decomposition runs starting at pressures above 5 mm., reproducibility of the pressure *vs.* time curves was poor and no definite order could be assigned to the reaction. The decrease of the rate in the latter half of the decomposition was very rapid. This effect is believed to result from products of the reaction acting as inhibitors. At pressures between 1.5 and 3 mm. (11 to 21 mm. of oil) the decomposition followed a second-order course up to 70% decomposition as shown in Fig. 1. Studies in this pressure range and at temperatures from 30 to 54° allowed the evaluation of the rate constant to be $k = 8.6 \times 10^{11} e^{-11,200/RT}$. A plot of ($\ln K - 2.813$) *vs.* $1/T$ is shown in Fig. 2 and the rate constants are given in Table I.

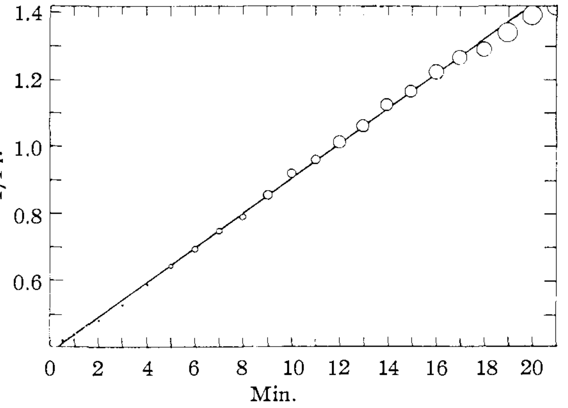

Fig. 1.—Typical second-order plot: non-inhibited decomposition, $P_r = P_{CF_3COOF}$, mm.

It was found that traces of oxygen, chlorine or bromine strongly inhibited the decomposition, thus suggesting a chain mechanism.

Two possible mechanisms have been used to account for the order and the products. In one the chain is carried by fluorine atoms, in the other by CF_3 radicals. The fluorine atom chain is

$$2CF_3COOF \longrightarrow CF_3COOF + CF_3COO + F \quad (1')$$
$$CF_3COOF + F \longrightarrow CF_4 + CO_2 + F \quad (2')$$
$$CF_3COO \longrightarrow CF_3 + CO_2 \quad (3')$$
$$2F + M \longrightarrow F_2 + M \quad (4')$$
$$2CF_3 \longrightarrow C_2F_6 \quad (5')$$

where M in step 4′ represents the wall.

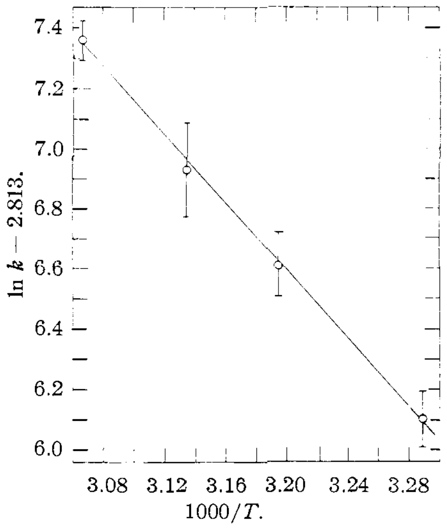

Fig. 2.—Arrhenius plot for non-inhibited decomposition in phosphate glass reactor.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR NON-INHIBITED DECOMPOSITION IN PHOSPHATE GLASS

Initial press. reactant, mm.	$K \times 10^{-3}$, cc. mole^{-1} sec.$^{-1}$	Initial press. reactant, mm.	$K \times 10^{-3}$, cc. mole^{-1} sec.$^{-1}$
31°		46°	
2.42	7.75	2.80	12.7
1.65	9.68	1.88	20.9
2.09	8.77	2.14	15.7
1.88	7.52	2.37	17.4
1.69	7.52	2.65	17.8
40°		53°	
2.34	15.3	2.85	24.7
2.66	10.0	2.19	29.5
2.22	12.2	2.20	24.5
2.66	12.6	2.06	26.4

Application of the steady-state condition to the fluorine atom concentration results in the following rate expression

$$-\frac{d(CF_3COOF)}{dt} = \left[K_1' + K_2'\sqrt{\frac{K_1'}{K_2'}}\right](CF_3COOF)^2$$

$$K_{obs} = K_2'\sqrt{\frac{K_1'}{K_4'}} = 8.6 \times 10^{11} e^{-11,200/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

The atom–radical abstraction in step (2) is similar to that proposed by Burton[5] in the photolysis of acetic acid, in which he found hydrogen atoms but no methyl radicals to be present.

The assumption that $K_1' \ll K_2' \sqrt{K_1'/K_4'}$ is based on results of studies of the inhibited decomposition discussed below.

The trifluoromethyl radical mechanism is

$$2CF_3COOF \longrightarrow CF_3COOF + CF_3 + CO_2 + F \quad (1)$$
$$CF_3 + CF_3COOF \longrightarrow CF_4 + CF_3 + CO_2 \quad (2)$$
$$2CF_3 \longrightarrow C_2F_6 \quad (3)$$

At steady state of CF_3 radicals the rate expression is

$$-\frac{d(CF_3COOF)}{dt} = [K_1 + K_2\sqrt{K_1/K_2}](CF_3COOF)^2$$

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[5] M. Burton, THIS JOURNAL, **58**, 1645 (1936).

where

$$K_{\text{obs}} = K_2\sqrt{\frac{K_1}{K_3}} = 8.6 \times 10^{11}e^{-11,200/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

the free radical mechanism is preferred for reasons to be discussed.

Inhibited Decomposition in Phosphate Glass Reactor.—In order to isolate the first step in the decomposition a number of runs were made at temperatures of 60 to 80° using chlorine and bromine as inhibitors. Essentially the same rate constants were obtained with either halogen, and it is believed that they served only to remove chain carriers. The rate constants are given in Table II.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR INHIBITED DECOMPOSITION IN PHOSPHATE GLASS

Initial press. reactant, mm.	Inhibitor	Initial press. inhibitor, mm.	$K \times 10^{-2}$ cc. mole^{-1} sec.$^{-1}$
		60°	
4.08	Cl_2	7.2	6.55
4.42	Cl_2	7.6	5.76
4.26	Br_2	5.8	7.59
7.59	Br_2	5.83	3.19
5.32	Br_2	9.42	5.34
		70°	
8.17	Cl_2	7.03	10.3
7.66	Cl_2	7.05	12.1
6.17	Cl_2	4.14	16.8
6.86	Cl_2	6.14	15.1
7.12	Cl_2	10.2	11.4
5.69	Br_2	8.03	16.3
6.45	Br_2	7.90	11.4
		75°	
4.71	Cl_2	7.28	31.4
5.32	Cl_2	7.70	28.4
5.95	Cl_2	7.99	26.4
		80°	
7.30	Cl_2	7.91	48.1
5.86	Cl_2	10.65	45.4

The decomposition was second order in respect to trifluoroacetyl hypofluorite and apparently was zero order in respect to the halogen pressure at the pressures used. Figure 3 shows a plot of $1/P$ vs. t for an inhibited decomposition reaction.

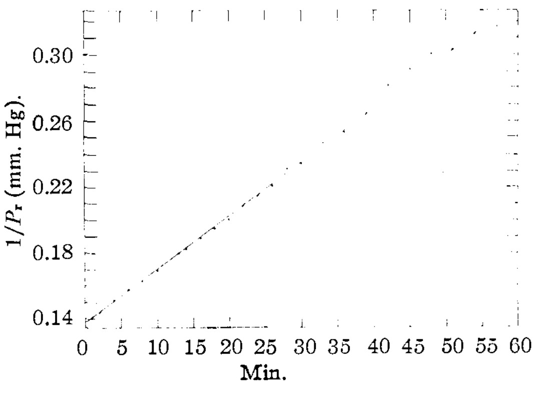

Fig. 3.—Second-order plot: inhibited decomposition, $P_r = P_{CF_3COOF}$, mm.

Analysis of the combined products from a number of runs with chlorine as inhibitor showed essentially equal amounts of CF_3Cl and CO_2. The pressure increase was equal to the initial pressure of trifluoroacetyl hypofluorite. Although analysis for ClF was not made because of experimental difficulties, there is little doubt that the over-all reaction was

$$CF_3COOF + Cl_2 \longrightarrow CF_3Cl + CO_2 + ClF$$

A series of reactions such as those below is believed to account for the inhibition.

$$2CF_3COOF \longrightarrow CF_3COOF + CF_3 + CO_2 + F \quad (6)$$
$$F + X_2 \longrightarrow XF + X \quad (7)$$
$$CF_3 + X_2 \longrightarrow CF_3X + X \quad (8)$$
$$2X + M \longrightarrow X_2 + M \quad (9)$$

The rate-determining step is assumed to be the activation step (6) and the activation energy will be a good approximation to the energy of the O–F bond in this compound.

It might be expected that step (2) in the CF_3 radical mechanism could compete quite successfully with step (8) above. The observed inhibition may be due to a large steric factor in step (2). Only a very small proportion of CF_4 was observed in the products of the chlorine inhibited reaction but this may be due to

$$CF_3 + ClF \longrightarrow CF_4 + Cl \quad (10)$$

as well as to step (2), since ClF apparently is a major product of the inhibited decomposition.

A plot of ($\ln K - 2.813$) vs. $1/T$ is shown in Fig. 4. The rate constant was found to be

$$K_1 = 1.33 \times 10^{19}e^{-25,000/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

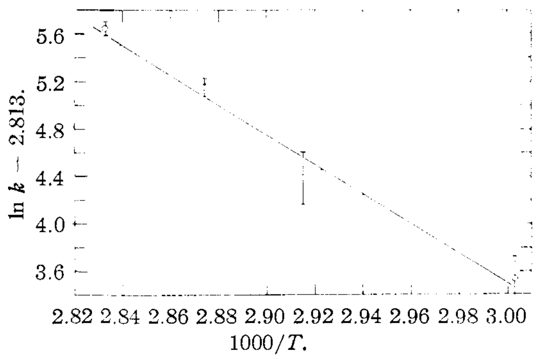

Fig. 4.—Activation energy plot–inhibited decomposition.

A halogen atom chain mechanism can be written which gives the same order but is considered unlikely since there is no reason to expect that chlorine and bromine atoms would give rate constants which are the same within experimental error.

The inhibited decomposition is, therefore, believed to be a unimolecular reaction in the second-order region. To explain the high frequency factor, activation in eleven square terms[6] (between 5 and 6 vibrational modes) must be assumed.

Energetics of Chain Steps.—For the fluorine atom chain $K_{\text{obs}} \approx K_2'\sqrt{K_1'/K_4'}$ and $E = 11.2 = E_2' + {}^1/_2 E_4' - {}^1/_2 E_4' = E_2' + 12.5 - {}^1/_2 E_4'$. Step

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[6] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3rd Ed., Clarendon Press, Oxford, 1933, p. 24.

(4) involves only the recombination of fluorine atoms and should proceed with approximately zero activation energy. Therefore $E_2' = -1.3 \approx 0$ kcal.

Similarly, for the trifluoromethyl radical chain $E = 11.2 = E_2 + {}^1/_2 E_1 - {}^1/_2 E_3$ and $E_2 - {}^1/_2 E_3 = -1.3 \approx 0$. Step (3) is the recombination of trifluoromethyl radicals and is also expected to require little activation energy. Hence $E_2 = -1.3 \approx 0$ kcal.

Step (2′) in the fluorine atom chain involves the rupture of a carbon–carbon bond. The energy of this bond in this compound has not been determined but is estimated to be at least 60 kcal. by comparison with the carbon–carbon bond in C_2F_6.[7] This step might reasonably be expected to have a positive activation energy.

The chain propagation step (2) in the free radical mechanism involves rupture of the much weaker (25 kcal. from inhibited decomposition) oxygen–fluorine bond and might be expected to have a correspondingly small activation energy. The energetics therefore tend to favor the free radical mechanism.

Effect of Surface.—The aluminum phosphate glass reactor, which was very sensitive to thermal strain, broke beyond repair before it could be packed for studies of the effect of increased surface area. Since no other such vessel could be obtained, a Pyrex reactor of similar dimensions and volume was substituted. Inhibited decomposition runs in this reactor at 70° were not reproducible. The non-inhibited decomposition was then studied at temperatures of 26 to 54° in this reactor. The second-order rate constant was found to be $K = 7.62 \times 10^{11}\ e^{-11{,}500/RT}$ cc. mole^{-1} sec.$^{-1}$. The reactor was then packed with aluminum phosphate glass rods with total surface area about equal to that of the reactor. The rate constant was then found to be $K = 2.04 \times 10^{10}\ e^{-8{,}900/RT}$ cc. mole^{-1} sec.$^{-1}$. The reaction was second order in both packed and unpacked Pyrex reactors at 1.5 to 3 mm. reactant pressure.

The observed activation energies, *i.e.*, 11.5 kcal. for the decomposition in the unpacked reactor and 8.9 kcal. for the packed reactor are within experimental error of each other and are not believed to indicate heterogeneity.

Considerable difficulty was encountered in obtaining reproducible rate constants for the non-inhibited decomposition in the aluminum phosphate glass reactor. The physical characteristics of the glass precluded "baking out" at high temperatures to remove adsorbed gases. The reactor was heated to 80° for 4–5 hours at pressures of 10^{-4} mm. or less but more drastic treatment was avoided. Chain termination by removal of trifluoromethyl radicals at the wall by adsorbed oxygen could have occurred to some extent and this effect may have been the cause of low values frequently observed for rate constants. The actual values of the rate constants in the unpacked Pyrex reactor were smaller than those in phosphate glass by a factor of approximately two. In the Pyrex reactor packed with phosphate glass the values were nearly the same as in the unpacked phosphate glass vessel. The rate constants in the phosphate glass alone often decreased by a factor as great as two after air had been admitted to the reactor. To avoid error due to such surface effects, runs made at a previously studied temperature were repeated to insure reproducibility before the thermostat was set at a different temperature.

The degree of heterogeneity has not been satisfactorily established but it is believed that the reaction was essentially homogeneous when run in the phosphate glass reactor after repeated use. If the reaction is homogeneous and if the first step is the rupture of the O–F bond the activation energy of 25 kcal. for the inhibited decomposition is the energy of the oxygen–fluorine bond in the compound.

Self-inhibition of Chain Reaction.—It was mentioned earlier that inhibition by products was suspected at pressures above 5 mm. A number of runs were made in which carbon dioxide, argon and the products from previous decompositions were added to the reactant. Addition of argon or carbon dioxide resulted in slightly higher values of rate constants while the combined reaction products showed a definite inhibiting effect.

The shapes of the pressure–time curves at pressure above 3 mm. strongly indicated inhibition. Such an effect could have been caused by oxygen formed from attack on the wall, either by trifluoroacetyl hypofluorite or by fluorine atoms produced in the initial decomposition step.

Carbonyl fluoride was present in all of the products which were analyzed and it was a major component among the products of decomposition in the presence of oxygen. This substance could have been formed by a series of reactions analogous to those which have been proposed for the reaction of methyl radicals with oxygen.[8,9] No CF_3OF could be identified by mass spectrum analysis, but a peak at mass 85 was always observed and ascribed to SiF_3^+. Isotope abundance confirmed this from accompanying peaks at masses 86 and 87 but the possible presence of a small amount CF_3O^+, also mass 85, cannot be excluded.

Further evidence of attack on the wall was furnished by the fall-off of pressure increase upon completion of reaction in a Pyrex reactor after continued use. After 100 runs in a Pyrex reactor at initial pressures of from 6 to 13 mm. the pressure increase upon completion of reaction had dropped from 1.9 to as low as 1.5 times the initial pressure. In the presence of excess oxygen the pressure increase was about 1.25. This difficulty was not encountered in the aluminum phosphate glass reactor at low pressures.

Chain Length.—The chain length of the non-inhibited decomposition, expressed as the ratio of the rate constant of the non-inhibited decomposition to that of the inhibited decomposition is $= 6.4 \times 10^{-8} e^{+13{,}800/RT}$. This results in high values of chain length. At 40°, $l = 275$; at 60°, $l = 73$.

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[7] B. S. Rabinovitch and John F. Reed (University of Washington), private communication.

[8] R. W. Hentz, THIS JOURNAL, **75**, 5810 (1953).

[9] A. D. Walsh, *Trans. Faraday Soc.*, **43**, 297 (1947).

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[CONTRIBUTION NO. 1332 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Quaternization Kinetics. II. Pyridine and 4-Picoline in Propylene Carbonate[1]

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The quaternization at 25, 50 and 75° of pyridine and 4-picoline by *n*-butyl bromide in propylene carbonate (dielectric constant, 65.1) follows second-order kinetics; at 25°, $k_2 = 2.59 \times 10^{-4}$ and 4.7×10^{-4} for pyridine and 4-picoline, respectively. Values of ΔE are 16.40 and 16.25 kcal./mole and of $\Delta S^{\ddagger}$, −30.0 and −29.0. Rates are slower than in tetramethylene sulfone, which has a lower dielectric constant.

The quaternization of several pyridine bases in tetramethylene sulfone has been found[3] to follow second-order kinetics accurately. In this paper, it will be shown that pyridine and 4-picoline also follow the same kinetics in propylene carbonate. The latter is a stable solvent of fairly high dielectric constant (65 at 25°) and appears to be a useful medium for quaternization reactions.

Experimental

Materials.—Pyridine, 4-picoline and *n*-butyl bromide were refractionated samples of C.P. reagents. **Propylene carbonate** (4-methyldioxolone-2) was purchased from the Jefferson Chemical Company. It was purified by distillation; b.p. 92° at 4.5 mm. The density ρ was determined in a 20-ml. pycnometer; $\rho(25°) = 1.197$; $\rho(50°) = 1.171$; $\rho(75°) = 1.144$. The dielectric constant was measured at 100 kc. in a guarded cell[4]; the value found was 65.1 at 25°.

Method.—Briefly described, solutions of base and of butyl bromide (about 0.1 *M*) were made up by weight, mixed and sealed into 2–3-ml. ampoules which were then immersed in thermostats at 25, 50 or 75°. At appropriate intervals, a tube was taken from the bath, and opened. Most of the contents were withdrawn by a hypodermic syringe, and the sample was then injected into 45 ml. of methanol and 6 ml. of aqueous 2 *N* sulfuric acid for potentiometric titration with 0.005 *N* silver nitrate solution. The weight of the sample was determined by difference in syringe weights.

Results and Discussion

The experimental results are summarized in Table I which gives temperatures, concentrations (b = moles base per gram of initial reaction mixture, a = moles butyl bromide per gram) and second-order rate constants k_2 in units (liters/mole min.). The latter were obtained as before[3] from the analytical data. Up to about 80% quaternization (beyond which the experimental error increases quite rapidly), the reaction follows second-order kinetics as shown by the linearity of plots against time of $xa(a - x)$ for $a = b$ or $\ln[b(a - x)/a(b - x)]$ for $a \neq b$; here x is concentration of bromide ion produced at time t. There was evidence for a minor side reaction: at about half reaction at 50 or 75°, an orange color developed; as the reaction proceeded, the color deepened to brown. The same color sequence at about the same rate appeared when picoline was heated with propylene carbonate; since the rate constants nevertheless remained constant, this side reaction does not interfere with the quaternization.

TABLE I

QUATERNIZATION BY *n*-BUTYL BROMIDE IN PROPYLENE CARBONATE

t, °C.	$10^4 b$	$10^4 a$	$10^3 k_2$
	Pyridine		
25	1.674	1.198	0.258
25	0.940	1.068	0.260
50	2.236	1.063	2.25
50	0.993	0.993	2.22
75	1.013	0.974	13.85
75	0.662	1.854	13.85
	4-Picoline		
25	0.922	1.076	0.479
25	.841	2.160	0.461
50	.758	1.191	3.97
50	.962	2.594	3.83
75	.670	0.987	24.6
75	.994	2.419	24.0

TABLE II

REACTION CONSTANTS

Cpd.	log A	ΔE	$\Delta S^{\ddagger}_{298}$
C_5H_5N	8.44	16.40	−30.0
C_6H_7N	8.69	16.25	−29.0

The reaction constants are given in Table II; they are defined by the familiar equation $k_2 = A \exp(-\Delta E/RT)$ and $\Delta S^{\ddagger}_{298} = R \ln A - 68.69$. On comparing with the rates in tetramethylene sulfone,[3] both pyridine and picoline are seen to react faster in tetramethylene sulfone than in propylene carbonate, despite the higher dielectric constant of the latter solvent. The ratios of the rates at 75° for pyridine and for picoline, respectively, are 1.69 and 1.65; at 25°, 1.79 and 1.78.

NEW HAVEN, CONNECTICUT

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(1) Office of Naval Research Project NR 051-002, Paper No. 49. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

(2) Results presented in this paper will be included in a thesis to be presented by Paul L. Kronick to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) B. D. Coleman and R. M. Fuoss, THIS JOURNAL, **77**, 5472 (1955).

(4) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).