It may be noted that the activation energy found here is higher than the values reported by others which ranged from about 36 kcal.[3b] to 39.9 kcal.[4] Because of the techniques employed here it is felt that the value 41,290 kcal. is the correct value for this reaction and that it may with justification be equated to the N–O bond energy in ethyl nitrate. The value for this bond energy has generally been taken as 34–37 kcal. per mole on the basis of studies on the nitrite esters. However the nitrite ester studies have met with some criticism[11] and the activation energies for the decomposition of these esters are still in some doubt.

The frequency factor found here, $10^{16.85}$ sec.$^{-1}$ is substantially higher than the value generally associated with first order reactions which is 10^{13} sec.$^{-1}$. In terms of the transition state theory this implies a high positive value for the entropy of activation, in this case a value of about 15 cal./mole. It has recently been reported by Szwarc[12] that frequency factors for many first order dissociations are of the order of 10^{14} to 10^{16} sec.$^{-1}$, so that there is no reason to consider the present case anomalous.

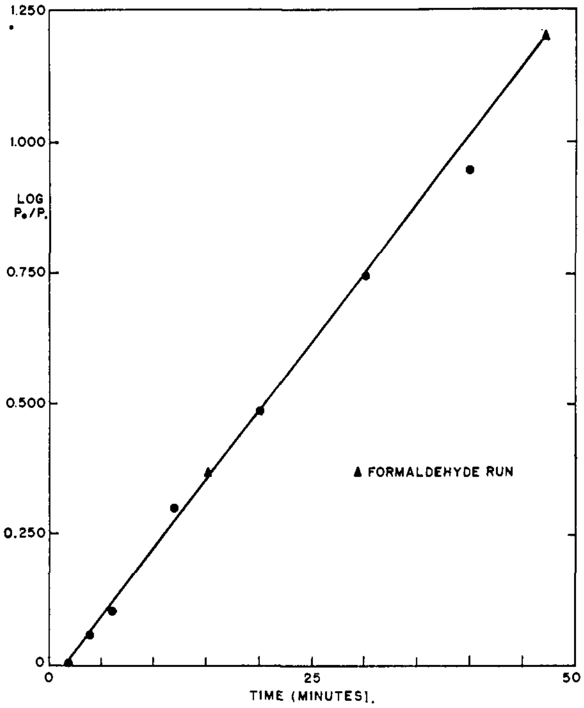

Fig. 1.—The rate of decomposition of ethyl nitrate at 181° in presence of nitric oxide and acetaldehyde.

Acknowledgments.—I would like to express my appreciation to Mr. Archie E. Davis for his help with some of the experimental work, to Dr. Robert M. Talley of the Solid State Division of this Laboratory for making a Perkin–Elmer Model 21 Double Beam Infrared Spectrometer available to me, and to Dr. Evan C. Noonan and Professor K. J. Laidler for helpful discussions on this work, which was carried out under Task Assignment Re2d-02-1 of the Bureau of Ordnance.

SILVER SPRING, MARYLAND

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(11) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

(12) M. Szwarc, *Disc. Faraday Soc.*, **14**, 125 (1953).

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

The Thermal Decomposition of Chloroform. I. Products[1a]

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RECEIVED JANUARY 6, 1954

The pyrolysis of gaseous chloroform has been investigated from 450 to 525°. The major products are hydrogen chloride and tetrachloroethylene. A variety of other chlorinated hydrocarbons have been identified and their relative abundances determined, using infrared techniques. Their genesis can be adequately described with a free-radical mechanism $CCl_3H \rightarrow CCl_2H\cdot + Cl\cdot$ (1), $Cl\cdot + CCl_3H \rightleftarrows HCl + CCl_3\cdot$ (2), $CCl_2H\cdot + CCl_3H \rightarrow CCl_2H_2 + CCl_3\cdot$(3), followed by displacement reactions, recombinations, disproportionations and dehydrochlorinations. The isotope exchange reaction of chloroform-*d* with hydrogen chloride was found to be rapid under conditions comparable to the pyrolysis experiments.

The thermal decomposition of chloroform was studied by Lessig.[2] He reported that the pressure–time curve was very irregular, and observed the formation of a "yellow crystalline material together with a tar." Verhoek[3] measured the pressure increase due to the pyrolysis of chloroform at 452 and 512°. He identified only hydrogen chloride as a product, but suspected the presence of hexachloroethane.

The present investigation consisted of a detailed study of the products of the thermal decomposition of chloroform. A concurrent investigation of the kinetics has been carried out; these results will be presented in paper II.

Experimental

A known quantity (approximately three millimoles) of purified[4] chloroform was introduced at a constant known rate into a carrier stream of purified helium gas and passed through a Vycor reaction chamber, packed with Vycor rings, which had previously been conditioned[5] (carbonized) by the equivalent of about one hundred runs.

The products in the exit gases were frozen out in a series

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(1) (a) Part of a Ph.D. dissertation submitted by G.P.S. to the Graduate School of Illinois Institute of Technology; (b) Lamp Development Laboratory, General Electric Co., Cleveland, Ohio; (c) University of Michigan, Ann Arbor, Michigan.

(2) E. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

(3) F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1525 (1935).

(4) C.P. chloroform was purified according to the procedure in Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948. Mass spectral and infrared examination of the product revealed no detectable impurities. For certain check experiments the chloroform was prepared directly from chloral, with identical results. Chloroform-*d* was synthesized from chloral and sodium deuteroxide. It was found to contain 1.6 ± 0.2% chloroform with no other impurities.

(5) R. J. Williams, *J. Chem. Soc.*, 113 (1953).

TABLE I

MATRIX[a] FOR INFRARED ANALYSIS

Wave no., cm.$^{-1}$	C_2Cl_6	CCl_2H_2	s-$C_2Cl_4H_2$	C_2Cl_3H	C_2Cl_4	C_2Cl_5H	$(100-X_{CCl_3H})$
680	0.126	0	0	0	0	0	−0.0115
1265	0	0.216	0.00599	0	0	0	− .00256
1279	0	0.0156	.0808	0	0	0	− .00149
840	0	0	.00799	0.818	0	0.0238	− .00216
912	0	0	.00328	.0365	1.526	0	− .000964
822	0.00808	0	.0316	.0324	0	0.541	− .00399
3025	0	0.00289	0.00553	0	0	0.00322	0.00750

[a] For 0.199 mm. matched cells. Units are mole per cent.

of traps at −195°. Hydrogen chloride was quantitatively separated from the other products and undecomposed chloroform by warming the traps to −107° (2,2,4-trimethylpentane bath) and flushing out with helium, through a tube containing crushed sodium hydroxide. The hydroxide was then neutralized in cold concentrated nitric acid, an excess of nitric acid added, and the solution made up to 100 ml. Aliquots of appropriate size were removed and titrated amperometrically with 0.01 N silver nitrate.[6a,b]

Separate experiments with known mixtures of hydrogen chloride and chloroform showed that no hydrogen chloride was retained in the −107° trap. In two runs the separated gas was collected, its pressure-volume product measured, and its infrared spectrum recorded. It was then absorbed in dilute sodium hydroxide, this solution acidified with nitric acid and titrated for chloride. The spectrum showed only hydrogen chloride. The quantity determined from the pressure–volume product agreed with the chloride titration value within ±1%.

The mixture of organic products was degassed and sealed *in vacuo* for later infrared analysis.[7] The matrix used is given in Table I. The row opposite 3025 cm.$^{-1}$ pertains to a method for obtaining solvent (chloroform) concentration independently of the other components. In this method the sample and reference cells are interchanged in the spectrometer light beams and the absorbency measured at 3025 cm.$^{-1}$ [8]

The products were identified by comparing the spectrum of the "products mixture" with the spectra of known compounds at the same concentrations in chloroform. The spectrum of the synthetic mixture did not differ significantly from the observed spectrum in any respect.

In certain experiments, the lighter products were removed by vacuum distillation. The residue was dissolved in carbon disulfide and the spectrum was obtained *vs.* carbon disulfide. This assisted in the identification of the heavy products, since the strong absorption of chloroform in the region 700–800 cm.$^{-1}$ was removed, allowing the observation of additional product bands.

In other experiments a static system was used to study the decomposition reaction. The apparatus consisted of a 250-ml. unpacked carbonized silica vessel joined to a Bodenstein quartz spiral gage and traps into which the products could be frozen and separated. The influence of added hydrogen chloride, tetrachloroethylene, hydrogen, etc., upon the rate of pressure rise was studied.

Pyrolyses of various compounds suspected of being intermediates were performed in sealed Pyrex vessels (300 ml.) placed in a furnace at 500° for short times. After quenching in liquid nitrogen, hydrogen chloride was distilled away from the organic compounds, which were held for infrared analysis.

Results and Discussion

Table II gives the results of four typical flow runs at different temperatures. Table III gives the material balances for each of these runs.

TABLE II

PRODUCT ANALYSES OF FOUR FLOW EXPERIMENTS[a]

Compound	Run 64 725°K.	Run 35 750°K.	Run 63 775°K.	Run 83 800 °K.
HCl	0.0346[b]	0.0865[b]	0.181[b]	0.408[b]
C_2Cl_4	.0065	.0272	.0395	.131
C_2Cl_6	.0018	.0069	.0192	.031
C_2Cl_5H	.0010	.0023	.0054	.0067
C_2Cl_3H	.0006	.0021	.0031	.0051
CCl_2H_2	.0006	.0012	.0035	.0031
s-$C_2Cl_4H_2$	.0003	.0008	.0015	.0030

[a] Contact time in the hot zone approximately 0.4 min.
[b] The numbers in the above table represent the number of millimoles of each of the products formed per millimole of chloroform introduced.

TABLE III

MATERIAL BALANCE CHECK

	Run 64	Run 35	Run 63	Run 83
HCl, g.	0.00381	0.00959	0.0201	0.0452
Organic cpds., g.	.3550	.3513	.3414	.3076
Total recovered, g.	.3588	.3609	.3615	.3528
Input CCl_3H, g.	.3607	.3632	.3635	.3629
Dif., %	−0.5	−0.8	−0.6	−2.8
Input CCl_3H mmoles	3.021	3.042	3.044	3.039
Recovered H	3.043	3.046	3.131	3.073
Dif., %	+0.8	+0.1	+2.9	+1.1
Recovered C	2.992	3.003	2.954	2.853
Dif., %	−1.7	−1.3	−3.0	−6.1
Recovered Cl	9.028	9.071	9.106	8.904
Dif., %	−0.4	−0.60	−0.3	−2.3

In addition to the products listed in Table II, others were found in amounts less than one-tenth the concentration of *sym*-tetrachloroethane. Some related compounds were found definitely to be absent. Hexachlorobenzene and vinyl chloride were identified with certainty. Carbon tetrachloride, 1,1-dichloroethylene, *cis*- and *trans*-dichloroethylene and dichloroacetylene were classed "probably present." In the category "probably absent" were

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[6] (a) H. A. Laitinen, W. P. Jennings and T. D. Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 355 (1946); (b) I. M. Kolthoff and P. K. Kuroda, *Anal. Chem.*, **23**, 1306 (1951).

[7] R. B. Bernstein, G. P. Semeluk and C. B. Arends, *ibid.*, **25**, 139 (1953).

[8] Using "reversed cells" (mixture in reference, solvent in sample beam), the measured absorbency is

$$A = kc_s d_s - d_r(kc_r + \sum_i k_i c_i)$$

where c_s = concentration of solvent in sample beam, c_r = concentration of solvent in mixture, c_i = concentration of component "i" in mixture, d_s = path length in sample cell, d_r = path length in reference cell, k = absorption coefficient of solvent, and k_i = absorption coefficient of component "i". For matched cells ($d_s = d_r = d$), and using mole per cent. units, this equation becomes

$$(100 - x_{CCl_3H}) = [A + \sum_i dk_i x_i]/kd$$

where x_{CCl_3H} = mole per cent. chloroform in mixture and x_i = mole per cent. component "i" in mixture. If $\sum_i k_i x_i \cong 0$, (small compared with A), then solvent concentration can be determined independently of the other components or by successive approximations using approximate values for the c_i's.

asym-tetrachloroethane, 1,1,1-trichloroethane and 1,2-dichloroethane. The following substances were found to be absent: hydrogen, chlorine, phosgene, formaldehyde, 1,2,4-trichlorobenzene, 2-chlorobutene-2, octachloropropane, *asym*-heptachloropropane, hexachloropropene, 1,2-dichloropropane, 1,2-dichloropropene-2, 1,1,2-trichloroethane, 1,1-dichloroethane, ethyl chloride, ethane, ethylene, chloroacetylene, acetylene, methyl chloride and methane.

Due to occasional overlapping absorption bands, it was not possible to prove the presence or absence of some compounds by infrared spectra alone. Thus some of the compounds are listed "probably present" on the basis of indirect additional evidence. It was not possible[7] to determine carbon tetrachloride by the infrared method, but mass spectral analysis for several runs indicated its presence in small amounts.[9] The identification of vinyl chloride was based on the band at 1599 cm.$^{-1}$. In attempting to duplicate the spectrum of a "products mixture," it was found that the appearance of this band could be more closely approximated by adding small quantities of 1,1-dichloroethylene (band at 1608 cm.$^{-1}$) and *cis*-dichloroethylene (band at 1584 cm.$^{-1}$). These, as well as *trans*-dichloroethylene, arise from the pyrolysis of 1,1,2-trichloroethane (Table IV) which is a possible intermediate in the decomposition of dichloromethane.

The compounds "probably absent" are so designated because their strong absorption bands should have appeared on the sides of the bands due to the major components, in spite of some overlap. The oxygenated compounds were considered, to determine if traces of oxygen had been present. Phosgene is always a major product of the oxidation of chloroform, while formaldehyde has been considered a minor product. No trace of oxygenated compounds was found in this investigation.

Table IV summarizes the results of the pyrolysis of various suspected intermediates.

TABLE IV

PYROLYSIS OF VARIOUS POSSIBLE INTERMEDIATES AT 500°

Compound	Major products	Relative rate[a]
Pentachloroethane	HCl, C_2Cl_4	Fast
sym-Tetrachloroethane	HCl, C_2Cl_3H	Very fast
Hexachloroethane	Cl_2, C_2Cl_4	Fast
Methylene chloride	HCl, C_2ClH_3, C_2Cl_3H	Very slow
Tetrachloroethylene	None	......
1,1,2-Trichloroethane	HCl, *cis*- and *trans*-$C_2Cl_2H_2$, CH_2CCl_2	Very fast
1,2-Dichloroethane	HCl, C_2ClH_3	Very fast
Trichloroethylene	HCl, unidentified brown deposit	Very fast

[a] Rate is relative to the pyrolysis of chloroform under similar conditions.

It is seen from Table II that with increasing extent of decomposition all products become of lesser importance when compared with hydrogen chloride and tetrachloroethylene, suggesting that the stoichiometry for the decomposition when run to completion might be $2CCl_3H \rightarrow 2HCl + C_2Cl_4$.

Three pressure-rise studies in the static system at 452° yielded an average $\Delta P/P_0$ of 0.460 ± 0.005, compared with the value of 0.5 predicted by the above equation. Verhoek[3] reported a value of 0.55. It should be noted that if appreciable amounts of other products of the type known to be present are formed, $\Delta P/P_0$ will become less than 0.5. Thus, for the equation

$$36CCl_3H \longrightarrow 32HCl + 13C_2Cl_4 + C_2Cl_5H + 2C_2Cl_6 + C_2Cl_4H_2 + C_2Cl_3H$$

one obtains $\Delta P/P_0 = 0.39$. The ratio of the number of millimoles of hydrogen chloride formed (at completion) to chloroform taken was found to be 1.00 ± 0.04, which confirms the simple over-all stoichiometry. The infrared spectrum of the organic products indicated tetrachloroethylene with only traces of other compounds.

In another series of experiments it was found that the rate of pressure rise was decreased by added hydrogen chloride. Added tetrachloroethylene enhanced the rate.

The following isotopic exchange experiment was conducted. A sample of 0.708 millimole of chloroform-*d* (98.4 atom per cent. deuterium) was allowed to decompose in the presence of 0.433 millimole of hydrogen chloride, at 452°, for a time of one half-life (based on pressure rise). The recovered chloroform was found to contain 66.8 atom per cent. deuterium, indicating appreciable isotopic exchange.

Kinetic runs in the flow system were also made with chloroform-*d*. It was found that the rate of decomposition of chloroform-*d* was approximately 20% less than that of ordinary chloroform. This small isotope effect is considered strong evidence that the primary step does not involve a C–H bond dissociation.

A mechanism which is qualitatively consistent with the above observations may be formulated as

Primary dissociation

$$CCl_3H \longrightarrow CCl_2H\cdot + Cl\cdot \tag{1}$$

Abstractions

$$Cl\cdot + CCl_3H \rightleftarrows HCl + CCl_3\cdot \tag{2}$$

$$CCl_2H\cdot + CCl_3H \longrightarrow CCl_2H_2 + CCl_3\cdot \tag{3}$$

The investigations of Urry, *et al.*,[13,14] on reactions of free radicals with chloroform, which indicate that the hydrogen atom is abstracted, lend support to reactions 2 and 3. A large variety of subsequent reactions involving the three free radicals and the substrate may then occur, including displacement reactions, recombinations, disproportionations and dehydrochlorinations. Some of the products expected would be *sym*-tetrachloroethane, pentachloroethane, hexachloroethane, carbon tetrachloride, trichloroethylene and tetrachloroethylene. The other products identified can be explained from

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[9] It should be noted that carbon tetrachloride, normally quite stable at high temperatures,[10] is much less stable in the presence of carbon,[11a, 11b] yielding chlorine, tetrachloroethylene, hexachloroethane and hexachlorobenzene.[12] It is therefore reasonable to expect that carbon tetrachloride would be only a minor product.

(10) P. Doty, *J. Chem. Phys.*, **12**, 399 (1944).

(11) (a) M. Bodenstein and P. Günther, *Z. angew. Chem.*, **43**, 423 (1930); (b) C. G. Fink and C. F. Bonilla, *J. Phys. Chem.*, **37**, 1135 (1933).

(12) V. V. Korshak, Y. A. Strepikheev and L. F. Verlatova, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1626 (1947); *C. A.*, **42**, 3721c (1948).

(13) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); THIS JOURNAL, **69**, 1100 (1947).

(14) W. H. Urry and J. R. Eiszner, *ibid.*, **74**, 5822 (1952).

subsequent reactions of the primary and secondary products above.[15]

The most important feature of the mechanism proposed is that the primary step is the rupture of a carbon–chlorine bond, not the carbon–hydrogen bond. The latter possibility was ruled out since a much larger isotope effect on the rate should have been observed when comparing a carbon–hydrogen with a carbon–deuterium bond scission. Newton and Rollefson,[22] who measured the relative rates of photochlorination of chloroform and chloroform-*d*, found a large isotope effect attributed to the step $Cl\cdot + CCl_3H \rightarrow CCl_3\cdot + HCl$. The result of the exchange experiment between chloroform-*d* and hydrogen chloride suggest that this step is a reversible one, confirming the opinion of Newton and Rollefson,[22] who found that chlorination of chloroform in the presence of deuterium chloride yielded some chloroform-*d*. A similar reaction between methyl radicals and hydrogen chloride has been reported.[23]

Catalysis by tetrachloroethylene is not easily explained, however. A possibility would seem to be the removal of trichloromethyl radicals, as[24]

$$CCl_3\cdot + C_2Cl_4 \longrightarrow CCl_3CCl_2CCl_2\cdot \qquad (A)$$

$$CCl_3\cdot + \cdot CCl_2CCl_2CCl_3 \longrightarrow 2C_2Cl_5\cdot \qquad (B)$$

$$C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot \qquad (C)$$

A more detailed discussion of the mechanism of the thermal decomposition of chloroform will appear in the forthcoming paper "II. Kinetics."

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The authors are indebted to Drs. H. E. Gunning, G. Gavlin, S. I. Miller, W. H. Urry and K. E. Howlett for helpful comments.

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[15] For example, vinyl chloride could arise from the pyrolysis of methylene chloride through a mechanism which involves abstraction, $Cl\cdot + CCl_2H_2 \rightarrow CCl_2H\cdot + HCl$ and the recombinations $2CClH_2\cdot \rightarrow C_2Cl_2H_4$, $2CCl_2H\cdot \rightarrow C_2Cl_4H_2$. Dehydrochlorination now gives vinyl chloride in one case and trichloroethylene in the other. Trichloroethylene was found as a product in the pyrolysis of methylene chloride. Several of the reactions in Table IV have received attention from other workers. Barton[16] examined the pyrolysis of pentachloroethane at 550° and Barton and Howlett[17] studied the dehydrochlorination of the isomeric tetrachloroethanes, giving some attention to the decomposition of trichloroethylene. Tetrachloroethylene is very stable toward polymerization.[18a, 18b] Williams[5] studied the dehydrochlorination of 1,1,2-trichloroethane, and Howlett[19] reported on the decomposition of 1,2-dichloroethane. The dimerization and polymerization of trichloroethylene has been studied by Henne and Ruh,[20] and by Schmerling and West.[18a] Dainton and Ivin[21] studied the pyrolysis of hexachloroethane.

[16] D. H. R. Barton, *J. Chem. Soc.*, 148 (1949).

[17] D. H. R. Barton and K. E. Howlett, *ibid.*, 2033 (1951).

[18] (a) L. Schmerling and J. P. West, THIS JOURNAL, **71**, 2015 (1949); (b) V. V. Korshak and N. G. Matveeva, *Doklady Akad. Nauk S.S.S.R.*, **85**, 797 (1952); *C. A.*, **47**, 28i (1953).

[19] K. E. Howlett, *Trans. Faraday Soc.*, **48**, 25 (1952).

[20] A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

[21] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 295 (1950).

[22] T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

[23] R. J. Cvetanovic and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158 (1953).

[24] The alternative, removal of hydrogen chloride, appears unlikely, since it is known[25] that hydrogen chloride will not add homogeneously in the gas phase to alkenes. On the other hand Schmerling and West[18a] found that in the benzoyl peroxide-induced addition of hydrocarbons to tetrachloroethylene, the yield of addition products decreased as the temperature was increased from 115 to 160°. In the present study no propanes were among the products, hence the addition of trichloromethyl radicals to tetrachloroethylene must be considered to lead to further reactions not regenerating trichloromethyl radicals.

[25] G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, **59**, 165 (1937).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The Exchange Reaction between Substituted Benzyl Iodides and Potassium Iodide. II. *p*-Nitrobenzyl Iodide[1]

BY E. LEE PURLEE, MILTON KAHN AND J. L. RIEBSOMER

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A measurable exchange has been observed in methanol and ethanol between the iodine atom in *p*-nitrobenzyl iodide and the iodide ion in potassium iodide. The exchange reaction was investigated over a temperature range from 0 to 30.9°. The total iodide concentration in methanol and in ethanol ranged from 0.000986 to 0.00609 *M* and 0.000983 to 0.00599 *M*, respectively. The rate laws for the exchange reaction are $R = 3.60 \times 10^{11} e^{-15,570/RT}(p\text{-}NO_2BzI)(KI)$ in methanol and $R = 5.42 \times 10^{12} e^{-16,460/RT}(p\text{-}NO_2BzI)(KI)$ in ethanol, where the units of R are moles liter^{-1} min.$^{-1}$.

Introduction

This paper represents the second in a series[2] of studies designed to obtain information regarding the influence of solvent and substituent on the mechanism and rate of the nucleophilic displacement reaction on carbon. The kinetics of the exchange reaction between *p*-nitrobenzyl iodide and potassium iodide in methanol and ethanol have been investigated. In each solvent the reaction was found to be first order with respect to both the *p*-nitrobenzyl iodide and potassium iodide.

Experimental

Radioactivity.—The 8.0-day I^{131} which was used as tracer in all experiments was extracted from neutron-irradiated tellurium metal. Solutions of potassium iodide in methanol and ethanol containing I^{131} activity were prepared as described previously.[2]

Chemicals.—*p*-Nitrobenzyl iodide was prepared according to the method of Finkelstein.[3] The crude product was twice crystallized from acetone and subsequently crystallized four times from absolute ethanol. Analysis of the product by the Volhard method of iodide determination[4]

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[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fulfillment of the requirements for the degree of Master of Science, in the Graduate School of the University of New Mexico, February, 1952, by E. Lee Purlee.

[2] P. Stillson and M. Kahn, THIS JOURNAL, **75**, 3579 (1953).

[3] H. Finkelstein, *Ber.*, **43**, 1531 (1910).

[4] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946, pp. 475, 573.