[Contribution from the Department of Chemistry, University of Rochester]

Photochemical Studies. LIII. Isopropyl Iodide[1]

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Isopropyl iodide gas when exposed to radiation at wave lengths of 3130 Å. or shorter gives propane, propylene, iodine and probably small amounts of hydrogen iodide. The ratio of propylene to propane always exceeds unity and no hexanes are found. Propylene and propane are not formed by disproportionation of isopropyl radicals but seem mainly to be formed by reaction of isopropyl radicals with isopropyl iodide: $i\text{-}C_3H_7 + i\text{-}C_3H_7I = C_3H_8 + C_3H_6 + I$. The excess of propylene seems to be due to a reaction involving iodine atoms. Illumination of mixtures of iodine vapor and isopropyl iodide at 5000 Å. absorbed only by the iodine gives strong supporting evidence for such a step and the following is suggested: $I + i\text{-}C_3H_7I = C_3H_6 + HI + I$. This type of reaction also occurs with other alkyl iodides. Use of mercury to remove iodine increases the ratio of propane to propylene but leads to an intensity effect which is due mainly to the slowness of diffusion of mercury vapor into the reaction zone. Addition of iodine in a mercury free system increases the ratio of propylene to propane. Quantum yields are well below unity. Possible explanations for this fact are discussed.

The photochemical reactions of simple alkyl iodides have been very extensively studied.[2] Recent work has been connected mainly with hot atom and hot radical effects and the detailed interpretation of the mechanism.[3]

It is generally assumed without completely conclusive evidence that the primary process leads to alkyl radicals and iodine atoms with a primary quantum yield of unity. The very low quantum yields usually observed are ascribed to secondary reactions some of which reform the original iodide.[4]

It was proposed to use the photochemical production of isopropyl radicals from isopropyl iodide as a means of studying the reactions of isopropyl radicals with oxygen. It became almost immediately evident that the mechanism in the absence of oxygen was not completely understood. The present study was undertaken to clarify some points in this problem. Quantum yields of iodine in isopropyl iodide vapor have been determined by West and Schlessinger,[5] whereas liquid isopropyl iodide has been studied by Emschwiller[6] and by McCauley, Hamill and Williams.[7]

Experimental

Isopropyl iodide was prepared by the method of Vogel.[8] The crude product was fractionated in a nitrogen atmosphere, transferred to a vacuum line and fractionated at low pressures. About one tenth of the crude product was retained. It was stored at the temperature of liquid nitrogen in a bulb in tandem with a gold foil trap and a U-tube immersed in liquid nitrogen to prevent entrance of mercury vapor. A portion of the compound was transferred to a mercury free line where it was stored at the temperature of liquid nitrogen. The purity exceeded 99.9% as indicated by the mass spectrometer and gas chromatography.

Propane and propylene were Phillips Research Grade. The purification of diethyl ketone already has been described.[9]

Acetone was Mallinckrodt "Analytical Reagent" grade and isopropyl alcohol was Eastman Kodak Co. "spectro" grade. Gas chromatography showed both to be sufficiently pure for use. The 2,3-dimethylbutane was Phillips "pure" grade and was fractionated and dried with calcium sulfate. Methyl, ethyl, *n*-propyl and *sec*-butyl iodides were Eastman Kodak Co. "White Label" products.

Iodine was Mallinckrodt Reagent grade purified by sublimation. Nitric oxide was obtained from Matheson Chemical Co. and was stated to be 98.7% pure. It was outgassed by pumping on it at the temperature of liquid nitrogen.

Two mercury arcs were used: a General Electric A-H6 high pressure lamp for experiments in which iodine absorbed the light and a British Thomson-Houston box type ME/D-250 watt lamp used for all other experiments.

Filter combinations were as follows: (1) for 2300–2900 Å.: 3 mm. of Corning Glass 9863 and 3 cm. of chlorine gas at a pressure of 740 mm.; (2) for 3130 Å. the filter suggested by Kasha[10]; (3) for 4000–5510 Å. a filter described by Bhagwat and Dhar[11]; (4) wave lengths below 5070 Å. were absorbed by 3 mm. of Corning Glass 3484; (5) for 5770–5790 Å. 1 cm. of a solution of 200 g./l. $CuSO_4 \cdot 5H_2O$ and 5 cm. of 20 g./l. $K_2Cr_2O_7$; (6) for 2950–4000 Å. 3 mm. of Corning Glass 9863 and 5 mm. of Pyrex.

Quantum yields at wave lengths of 3130 Å. and below were based on internal actinometers of diethyl ketone or acetone at 120° where carbon monoxide yields are unity. Intensities and fractional absorptions were determined either with a photocell (RCA Model 935)-Galvanometer or a photocell potentiometer–recorder system. Neutral density filters and wire screens were used at various times to vary intensity.

Two separate vacuum lines were used, one a conventional type and the other essentially mercury free. A McLeod gauge–Toepler pump combination previously described[12] was used to collect and measure gases. A small mercury diffusion pump was used to transfer gases from the reaction cell to the McLeod gauge part of the system. The cell section consisted of the quartz cell and a magnetically driven stirrer.

The propane–propylene fraction was removed at −130°, measured by the McLeod gauge and transferred to a mass spectrometer tube. The fraction condensable at −130° included excess isopropyl iodide. It was condensed in a sample tube and analyzed by gas chromatography.

It is difficult to construct a line completely free of mercury, but in the present experiment traces of mercury would be removed by the iodine. The quartz reaction cell was isolated by a stopcock from the rest of the apparatus. This stopcock was lubricated with polybutene[13] for the experiments with added iodine. This grease is not seriously at-

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(2) For a review up to 1939 see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 334. A complete survey of work on these reactions is given by E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 397.

(3) See D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, This Journal, **78**, 6228 (1956), and other articles by Hamill, Williams and collaborators.

(4) See E. W. R. Steacie, ref. 2, p. 397.

(5) W. West and L. Schlessinger, This Journal, **60**, 961 (1938).

(6) G. Emschwiller, *Ann. chim.*, **17**, [10] 413 (1932).

(7) C. E. McCauley, W. H. Hamill and R. R. Williams, Jr., This Journal, **76**, 6263 (1954).

(8) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 283.

(9) A. N. Strachan, Ph.D. Thesis, University of Rochester, 1954.

(10) M. Kasha, *J. Am. Opt. Soc.*, 929 (1948).

(11) W. V. Bhagwat and N. R. Dhar, *J. Phys. Chem.*, **35**, 2391 (1931).

(12) A. N. Strachan and W. A. Noyes, Jr., This Journal, **76**, 3258 (1954).

(13) Kindly furnished by Dr. W. D. Walters.

tacked by iodine, but it has a high softening temperature. For other runs "Spectrovac" Type II grease produced by Robert R. Austin was used. Pressures were read by an RCA-1946 thermocouple gauge. A three stage silicone oil diffusion pump was used to evacuate the system. Gases were removed through a stopcock to a line which contained mercury but always separated from the stopcock by a U-tube immersed in liquid nitrogen.

Isopropyl iodide was distilled from the storage bulb, condensed in a U-tube at −130° and then distilled from one trap to another with continued pumping. The U-tube was placed in water to give the right vapor pressure of isopropyl iodide.

Analyses for iodine were made by condensing the liquid fraction in a 5-ml. bulb, adding potassium iodide solution, and titrating with sodium thiosulfate.

Propane–propylene mixtures were analyzed with the mass spectrometer.

Results

(a) Photochemical Dissociation of Iodine in the Presence of Alkyl Iodides.—At a temperature of 35°, the illumination of mixtures of 0.4 mm. iodine with ethyl iodide, *n*-propyl iodide, *sec*-butyl iodide and isopropyl iodide with light from the A-H6 lamp transmitted by filter No. 4 resulted in production of the alkenes in the ratios 1:5:21:22. Methyl iodide gave no detectable products. The corresponding alkanes were within experimental error of zero and in some experiments truly zero. Only negligible amounts of hydrocarbons were formed in thermal blanks and upon irradiation of the pure alkyl iodide. The relative reactivities are only approximate, since the pressures of the various iodides were not kept constant. Propylene was also formed by illumination of iodine–isopropyl iodide mixtures with the radiation filtered through combinations 3 or 5. About one-eighth as much propylene is formed with the latter filter as with filter No. 4, but a rough calculation based on the extinction coefficients of iodine[14] together with the transmittances of the filters and the wave length distribution of energy supplied by the General Electric Company for the A-H6 lamp shows that quantum yields in the two regions are not very different. The ratio of butene-2 to butene-1 from *sec*-butyl iodide was 3.4 and 3.7 to one in two experiments. The butene-2 was at least 85% the *trans*-isomer. The rate of propylene formation from isopropyl iodide was unaffected by the presence of 75 mm. of dry air.

TABLE I

PHOTOLYSIS OF ISOPROPYL IODIDE IN THE ABSENCE OF MERCURY. EFFECT OF INTENSITY AND OF NITRIC OXIDE

$T = 35°$; $\lambda = 3130$ Å. (filter 2); cell and cell system volumes, as in Fig. 1; pressure of isopropyl iodide 39 mm.

I_a, quanta/ml./sec. $\times 10^{-12}$	Time, min.	$\Phi_{C_3H_6}$	$\Phi_{C_3H_8}$
37.1	32.5	0.10	0.07
29.3	34.5	.10	.07
12.4	120	.09	.05[a]
11.6	166	.10	.06
3.2	300	.13	.05
0.59	1055	.14	.07
37	23	.16	.00[b]

[a] $\Phi_{I_2} = 0.05$. [b] 80 mm. nitric oxide present; $\Phi_{I_2} = 0.49$.

(b) Photochemical Decomposition of Isopropyl Iodide.—Hydrogen, methane and 2,3-dimethylbutane were not among the products of isopropyl iodide in the absence of mercury at constant intensity. Only after extended photolyses do the rates show a decrease. The per cent. decomposition was kept in the linear region in experiments for intensity dependence, shown in Tables I and II.

In the presence of added iodine, propane is greatly decreased, especially at the longer wave lengths, as shown in Table III, but increases after long photolysis. In the photolysis in the presence of mercury and 0.5 mm. oxygen, propane is almost completely suppressed.[15]

TABLE II

PHOTOLYSIS OF ISOPROPYL IODIDE IN THE PRESENCE OF MERCURY. EFFECT OF INTENSITY

$T = 35°$; pressure of isopropyl iodide, 36 mm.; filter 2; $\lambda = 3130$ Å. cell volume 144.2 ml.; volume of cell, stirrer and connecting tubing 438 ml.

I_a, quanta/ml./sec. $\times 10^{-12}$	Time, min.	$\Phi_{C_3H_6}$	$\Phi_{C_3H_8}$
27.4	60	0.13	0.12
24.3	60	.13	.13
7.84	120	.16	.14
2.7	120	.24	.23

TABLE III

PHOTOLYSIS OF ISOPROPYL IODIDE. EFFECT OF ADDED IODINE

$T = 35°$; volumes as in Fig. 1; filter 2 except where indicated; $\lambda = 3130$ Å.

Pressure i-C_3H_7I, mm.	Pressure I_2, mm.	Time, min.	Rate C_3H_8, molecule/ml./sec. $\times 10^{-12}$	$\frac{\text{Rate } C_3H_6}{\text{Rate } C_3H_8}$
39[a]	0	15	3.0[b]	4.4
39[a]	0.39	6	1.1	11.0
39[a]	0.43	61	3.0	3.3
70	0	300	0.063	2.6
70	0.43	300	0.0095	15.0

[a] Pyrex glass omitted from filter. [b] Rate iodine = 3.0×10^{12} molecules/ml./sec.

Discussion

For the sake of convenience all of the reactions to be mentioned will first be listed

$$i\text{-}C_3H_7I + h\nu = i\text{-}C_3H_7 + I \qquad (1)$$
$$i\text{-}C_3H_7 + I_2 = i\text{-}C_3H_7I + I \qquad (2)$$
$$i\text{-}C_3H_7 + I = i\text{-}C_3H_7I \qquad (3)$$
$$= C_3H_6 + HI \qquad (4)$$
$$2\ i\text{-}C_3H_7 = C_3H_6 + C_3H_8 \qquad (5)$$
$$= C_6H_{14} \qquad (6)$$
$$i\text{-}C_3H_7 + i\text{-}C_3H_7I = C_3H_6 + C_3H_8 + I \qquad (7)$$
$$I + i\text{-}C_3H_7I = C_3H_6 + HI + I \qquad (8)$$
$$i\text{-}C_3H_7 + HI = C_3H_8 + I \qquad (9)$$
$$I + I + M = I_2 + M \qquad (10)$$

Primary process 1 almost certainly has a quantum yield of unity. Evidence for this is found in the following facts: (1) the quantum yield of iodine formation is about 0.5 in the presence of nitric oxide; (2) scavengers which remove iodine (*e.g.*, mercury and silver) cause quantum yields in all of the simple alkyl iodides to rise toward unity.

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[14] R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953).

[15] G. R. McMillan, to be published.

Reactions 2 and 3 which reform isopropyl iodide must be mainly responsible for low quantum yields. Mercury vapor was used in the present experiments to remove iodine. Since mercury vapor reacts rapidly with iodine atoms and molecules, reactions 2 and 3 will be prevented only to the extent that mercury can diffuse into the reaction vessel. The effective mercury vapor concentration will be lower the higher the intensity thus leading to an apparent effect of intensity on the quantum yields. In the absence of mercury there is no effect of intensity on the yields.

The absence of an intensity effect must mean that (2) and hence (3) occur on the walls at least until the I_2 pressure in the gas phase has become appreciable. Quantum yields must be determined by the competition between (7) and diffusion of C_3H_7 radicals to the walls. With added iodine at 0.3–0.4 mm. pressure reaction 2 must occur mainly in the gas phase.

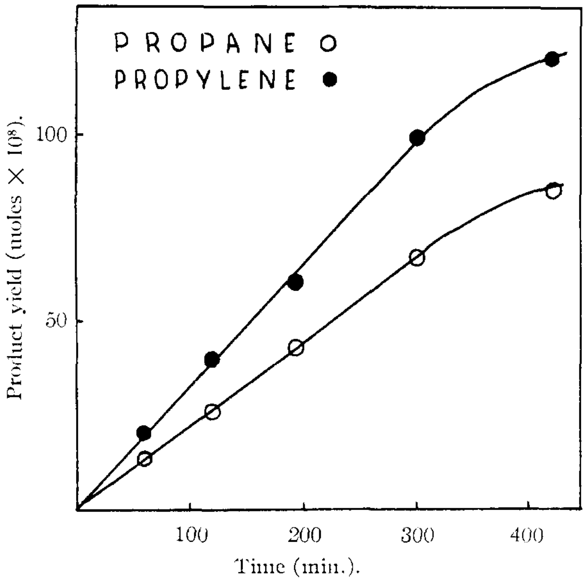

Fig. 1.—Product yields at 35°; pressure of isopropyl iodide, 39 mm.; light source, B.T.-H. and filter No. 6; cell volume, 86.5 ml.; volume of cell and connecting tubing, 114 ml.; iodine-free system.

Propane, propylene and iodine are the only observed products. Hydrogen iodide could not be determined but must be formed.

Others have found the ratio of the rate of (5) to the rate of (6) to be about 0.5[16,17] at room temperature. 2,3-Dimethylbutane was not found as a product. This affords almost conclusive evidence that (5) and (6) do not occur during photolysis of isopropyl iodide.

Propylene and propane are formed in approximately equal quantities at low intensities in the presence of mercury vapor. This suggests that these products are formed by reaction 7. Possibly this reaction occurs in two steps: an abstraction to form C_3H_8 and a dissociation of the C_3H_6I radical to give $C_3H_6 + I$. No evidence for writing the reaction in two steps is found in the present work. For reasons given later reaction 8 is almost certainly not a two-step process.

In the absence of mercury vapor the yield of propylene always exceeds the yield of propane (Table I). Nitric oxide, which should remove isopropyl radicals effectively, also causes the yield of propane to be zero within experimental error (Table I).

The relative rates of (2) and (7) at 35° can be estimated from the data in Table III. This is done from the equation

$$\frac{R_P^0}{R_P} = 1 + \frac{k_7}{k_2}\frac{(I_2)}{(C_3H_7I)} \qquad (11)$$

where R_P^0 is the rate of propane formation in the absence of iodine and R_P is the rate of propane formation in the presence of iodine under otherwise identical conditions. At 3130 Å. $k_7/k_2 = 520$. With a broad range of wave lengths greater than about 2300 Å. the apparent value of k_7/k_2 is 170. This indicates an apparent "hot radical" effect and that (7) probably has an appreciable activation energy. The value obtained at 3130 Å. should approximate the correct value for thermally equilibrated isopropyl radicals. The activation energy difference $E_7 - E_2$ could not be obtained because of thermal reaction and wall effects.

Yields are linear functions of time (Fig. 1) except for long runs when iodine begins appreciably to accumulate in the gas phase. For very long runs (not shown) the yield of propane increases again slightly. This is almost certainly due to reaction 9 which would occur if hydrogen iodide were present.

Since propylene is always formed in excess of propane except when mercury vapor is present, there must be some other reaction than (7) which yields propylene. The data indicate strongly that this must be connected in some way with iodine atoms and reaction 8 is a possibility. In the liquid phase reaction 4 has been suggested by Bunbury, Williams and Hamill.[3] Presumably this reaction could occur in a "cage," but under the experimental conditions used here it would be relatively unimportant in the gas phase.

Iodine shows a convergence limit at 4995 Å.[18] Below this wave length absorption in the continuum leads to $^2P_{1/2}$ and $^2P_{3/2}$ atoms. Evidence from the present work does not show whether atoms in these two energy states have different reactivities. At wave lengths longer than 4995 Å. excited iodine molecules predissociate into normal $^2P_{3/2}$ atoms by collision.

Mixtures of iodine and isopropyl iodide illuminated by wave lengths absorbed only by the iodine show propylene to be formed whereas propane formation was always within experimental error of zero. These data provide strong evidence in favor of a reaction such as (8).

If (8) occurs in isopropyl iodide, similar reactions may well occur in other alkyl iodides which can yield alkenes in single step processes. Thus methyl iodide should be an exception. These pre-

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(16) F. E. Blacet and J. G. Calvert, This Journal, **73**, 661 (1951).

(17) R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953).

(18) See A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Dover Publications, Inc., New York, N. Y., 1950, p. 65.

dictions are indeed verified by the data. Relative rates are C_2H_5I:*n*-C_3H_7I:*sec*-C_4H_9I:*i*-C_3H_7I::1:5:21:22.

Reaction 8 as written is similar to the bimolecular elimination reaction (E_2) known to occur in solution. As an ionic process it occurs as a concerted single step reaction.[19] With secondary butyl iodide one would predict *trans*-butene-2 to be formed from an E_2 reaction. In the present work *trans*-butene-2 constituted at least 85% of the butene formed from secondary butyl iodide. Probably reaction 8 also occurs as a concerted single step reaction.

The mechanism proposed to explain the present data is based mainly on (1), (2), (7) and (8). Reaction 3 and possibly reaction 4 may occur to some extent on the walls. Reaction 9 may occur if hydrogen iodide is allowed to accumulate. Evidence in favor of (1), (2), (7) and (8) being the important steps is very strong but not in all cases absolutely conclusive.

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[19] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

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

The Kinetics of the Exchange of Chlorine between Hydrogen Chloride and Acetyl Chloride in the Vapor Phase[1]

BY WARREN J. NEILL AND MILTON KAHN

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A measurable exchange has been observed between hydrogen chloride and acetyl chloride in the vapor phase. The exchange reaction was investigated over a temperature range from 0 to 29.6°; the concentration of acetyl chloride ranged from 0.0026 to 0.0106 *M* and of hydrogen chloride from 0.0031 to 0.0080 *M*. Over the range of conditions studied the rate of exchange can be represented by $R = 0.17e^{-1550/RT}(\mathrm{HCl})(\mathrm{CH_3COCl})$ where the units of *R* are liter × mole^{-1} × sec.$^{-1}$. A more complicated rate expression cannot be excluded but is not called for by the data.

Introduction

This paper is concerned with the kinetics of the exchange of chlorine atoms between hydrogen chloride and acetyl chloride in the vapor phase. The reaction was found to be first order with respect to each reactant and homogeneous.

Experimental

Radioactivity.—The 3.08 × 10^5-year chlorine-36, which was used as tracer in all experiments, was obtained from Oak Ridge in the form of a dilute solution of hydrochloric acid (5.5 ml. of 0.37 *M* hydrochloric acid contained 20 μc. of chlorine-36).

Chemicals.—Merck reagent grade acetyl chloride was further purified according to the method of Fieser.[2] All other chemicals were of analytical grade and were used without further purification. Standard active solutions of potassium chloride were prepared by inoculating weighed amounts of potassium chloride with the active hydrochloric acid solution and diluting to volume.

Procedure.—Reaction mixtures of hydrogen chloride and acetyl chloride were prepared employing ordinary vacuum-line techniques. Purified acetyl chloride was fractionally distilled under vacuum and allowed to vaporize at a pressure determined by an appropriate constant-temperature bath; the vapor was frozen in a trap prior to the introduction of hydrogen chloride.

Radioactive hydrogen chloride, generated by adding sulfuric acid to dry, radioactive potassium chloride, was passed over phosphorus pentoxide before being admitted to the reaction vessels and subsequently frozen in the trap with the acetyl chloride. The frozen mixture was allowed to vaporize and diffuse into the reaction vessels over a period of 30 minutes, at room temperature, in the presence of red light. The reaction vessels which were inverted U-tubes were isolated from each other with stopcocks and sealed off from the vacuum line after freezing the reactants with liquid nitrogen. Only about 30 seconds were required to freeze the contents of eight tubes. The sealed tubes were immersed in a constant-temperature water-bath and allowed to come to thermal equilibrium over a period of 30 minutes. Zero time was reckoned from the time the first sample was taken from the bath. In most instances the reaction was allowed to proceed to within 65–84% of completion.

The concentrations of the reactants in each experiment were determined by dissolving the contents of each of two reaction vessels of known volume in water and analyzing the resulting solution for total hydrogen ion and chloride ion.

Separation Procedure.—Acetyl chloride was condensed in one arm of the U-tube with a Dry Ice–acetone bath; the hydrogen chloride was frozen in the other arm with a liquid nitrogen bath. The arm containing the acetyl chloride was then cracked and immersed immediately in water. The purity of the separated acetyl chloride proved to be greater than 99%; the separated hydrogen chloride fraction was contaminated with acetyl chloride. The fraction exchange in each instance was calculated from the activity in the separated acetyl chloride. For most of the runs the half-time for exchange was determined on the basis of five samples.

Measurement of Radioactivity.—The chlorine-36 activity was detected according to the procedure of Kahn, Freedman, Feltham and Lark[3] which is based on the precipitation of mercurous chloride. The samples were placed directly below the 4.8-mg./cm.^{2} dural window of a methane-flow proportional counter operated at atmospheric pressure and 4,200 volts. A model PA-1 pulse amplifier fed into a model SC-2 scaler supplied by the Los Alamos Scientific Laboratory.

Results and Discussion

The reaction studied is

$$\mathrm{CH_3COCl(g) + HCl^*(g) = CH_3COCl^*(g) + HCl(g)}$$

where the asterisks indicate radioactive atoms. The constant rate of exchange *R* of chlorine atoms between acetyl chloride and hydrogen chloride in any one experiment was evaluated with the aid of the logarithmic form of the isotopic exponential ex-

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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 Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1957, by Warren J. Neill.

[2] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 380.

[3] M. Kahn, A. J. Freedman, R. D. Feltham and N. L. Lark, *Nucleonics*, **13**, 58 (1955).