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

Methylene Derivatives as Intermediates in Polar Reactions. XIII. The Basic Hydrolysis of Bromochloroiodomethane[1]

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Bromochloroiodomethane may be prepared conveniently by the action of alkali and sodium iodide on dibromochloromethane in methanol. The kinetics of its hydrolysis in water and $66^2/_3\%$ dioxane–water have been studied. The reaction involves the reversible formation of a trihalomethyl carbanion followed by a slower decomposition of the carbanion to dihalomethylenes. Each of the two intermediates, bromochloromethylene and chloroiodomethylene, is formed to a considerable extent. The reaction (as measured by the rate of disappearance of alkali) is slowed by the addition of iodide ions which capture the dihalomethylenes and transform them to bromochloroiodomethane and chlorodiiodomethane, respectively. From a knowledge of the concentrations of the two haloforms (determined by extraction and infrared analysis) and the efficiency with which iodide ion captures the two dihalomethylenes (determined by separate experiments on dibromochloromethane and chlorodiiodomethane) the extent to which the reaction followed each of the two major paths was determined. The resultant data provided a new type of check on the applicability of a previously-published equation for correlating haloform hydrolysis rates and also permitted an "improvement" of the parameters used in the equation.

Introduction

For those haloforms whose alkaline hydrolysis has the mechanism

$$\mathrm{CHXYZ} + \mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CXYZ}^- + \mathrm{H_2O} \quad (1)$$

$$\mathrm{CXYZ}^- \xrightarrow{k_2} \mathrm{CXY} + \mathrm{Z}^-$$

an equation has been suggested for the quantitative correlation of hydrolysis rates.[2] This equation has the form

$$\log \frac{(k_2/k_{-1})_{\mathrm{CHXYZ}}}{(k_2/k_{-1})_{\mathrm{CHCl}}} = M_{\mathrm{X}} + M_{\mathrm{Y}} + N_{\mathrm{Z}} + \log \frac{n_{\mathrm{Z}}}{3} + (c - d) \log \frac{k_1^{\mathrm{CHXYZ}}}{k_1^{\mathrm{CHCl_3}}} \quad (2)$$

where the M's are parameters for the ability of the halogen in question to stabilize the dihalomethylene being formed, N depends on the ability of Z to be lost as an anion and $(c - d)$ relates to the carbanion character of the transition state. Combination of the predicted (k_2/k_{-1})'s with the known or estimable values[3] of k_1 yields the hydrolysis rate constants. All of the haloforms studied previously hydrolyzed to yield essentially only one dihalomethylene. Since eq. 2 should, in principle, be capable of predicting the rate of formation of each of the various possible dihalomethylenes, we decided to study a haloform in which two dihalomethylenes were formed to a significant extent. From the magnitude of the parameters determined previously it appeared that bromochloroiodomethane would be such a compound.

Results and Discussion

Preparation of Bromochloroiodomethane.—Since the only published preparations of bromochloroiodomethane[4] appear to be rather tedious we devised a new synthesis. The formation of dichloroiodomethane from chloroform, alkali and sodium iodide already has been reported.[5] Although the dichloroiodomethane was prepared in such a manner as to give evidence concerning a reaction mechanism, this type of reaction, the capture of a dihalomethylene by a halide ion to give a carbanion that is then protonated, can be developed into a fairly general method for the preparation of haloforms by consideration of the following factors. The halide ion should be present in high concentration so as to compete effectively for the dihalomethylene. The solvent should be capable of dissolving large amounts of halide ions, haloform and at least some alkali. The starting haloform should be as reactive as possible toward basic hydrolysis, compared to the haloform to be produced. Information on these and other relevant points can be found in earlier articles in this series. The bromochloroiodomethane was prepared from sodium iodide, dibromochloromethane and sodium methoxide in methanol solution. The properties of the product are in good agreement with those that would be expected, although not in such good agreement with those reported by Garino and Teofili.[4]

Hydrolysis Kinetics.—For reasons of the type described previously for other haloforms[2,3,5] (mass-law effect, reactivity, analogy) it seems assured that bromochloroiodomethane hydrolyzes by the dihalomethylene mechanism. Since the k_1's for bromoform and iodoform are within the experimental uncertainty of each other as are the k_1's for bromodichloromethane and dichloroiodomethane,[3] we would expect k_1 for bromochloroiodomethane to be essentially equal to that for dibromochloromethane. If this is anywhere near the truth then the equilibrium formation of the trihalomethyl anion, as in eq. 1, must be quite fast compared to the dihalomethylene formation, which should occur, to a considerable extent, in each of two different ways

$$\mathrm{CBrClI}^- \xrightarrow{k_2} \mathrm{CBrCl} + \mathrm{I}^-$$

$$\mathrm{CBrClI}^- \xrightarrow{k_3} \mathrm{CClI} + \mathrm{Br}$$

with the formation of bromoiodomethylene by loss of chloride ion being a negligible side reaction. From this mechanism the hydrolysis in dilute

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(1) Abstracted from the M. S. thesis of F. P. Prosser, Georgia Institute of Technology, 1958. For article XII in this series see J. Hine and K. Tanabe, THIS JOURNAL, **80**, 3002 (1958).

(2) J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958).

(3) (a) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957); however, *cf.* (b) J. Hine, R. Butterworth and P. B. Langford, *ibid.*, **80**, 819 (1958).

(4) M. Garino and I. Muzio, *Gazz. chim. ital.*, **52**, 226 (1922); M. Garino and E. Teofili, *ibid.*, **56**, 847 (1926).

(5) J. Hine and A. M. Dowell, Jr., THIS JOURNAL, **76**, 2688 (1954).

aqueous solution, where essentially all of the dihalomethylene is hydrolyzed, should be a second-order reaction for which the rate constant has the significance

$$k_h^{\mathrm{CHBrClI}} = \frac{k_1(k_2 + k_3)}{k_{-1}} \qquad (3)$$

From studies of the alkaline hydrolysis of bromochloroiodomethane in water and aqueous dioxane, satisfactory second-order rate constants were determined and are listed in Table I. Some needed data on chlorodiiodomethane also are listed in this table.

TABLE I

KINETIC DATA ON THE HYDROLYSIS OF CHBrClI AND $CHClI_2$ IN AQUEOUS SOLUTION

Haloform	Temp., °C.	10^3k, l. mole^{-1} sec.$^{-1}$
CHBrClI	50.0	5.53 ± 0.28
CHBrClI	30.0	0.266 ± .014
CHBrClI	50.0	2.6 ± .2[a]
CHBrClI	50.0	10.45 ± .29[b]
$CHClI_2$	64.5	5.92 ± .17[c]
$CHClI_2$	64.5	1.556 ± .05[d]

[a] In the presence of 0.15 *M* NaI; falling rate constants extrapolated to zero time. [b] In $66^2/_3\%$ dioxane-$33^1/_3\%$ water (vol.). [c] In the presence of 0.15 *M* $NaNO_3$ and 0.15 *M* $NaClO_4$. [d] In the presence of 0.30 *M* NaI.

For bromochloroiodomethane in water a heat of activation of 28.9 ± 1.0 kcal./mole and an entropy of activation of +20.5 ± 2.2 e.u. may be calculated from the equation[6]

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

The slowing of the hydrolysis of chlorodiiodomethane by sodium iodide observable from Table I must be a mass-law effect[3b,5] in which iodide ions capture chloroiodomethylene intermediates and revert them to haloform.

$$CHClI_2 + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CClI_2^- + H_2O$$

$$CClI_2^- \underset{k_3^{\mathrm{I}}}{\overset{k_5}{\rightleftharpoons}} CClI + I^- \qquad (4)$$

$$CClI + H_2O \xrightarrow{k_3^{\mathrm{W}}} H_2\overset{\oplus}{O}\text{-}\overset{\ominus}{C}ClI \xrightarrow{\text{fast}} CO \text{ and } HCO_2^-$$

By use of the equations derived previously[5] the magnitude of the mass-law constant (r_3) may be calculated from the rate constants in the presence and absence of iodide ions.

$$r_3 = k_3^{\mathrm{I}}/k_3^{\mathrm{W}} = 9.34$$

The Hydrolysis of Bromochloroiodomethane in the Presence of Sodium Iodide.—While the halide ions liberated from the haloform, like the hydroxide ions also present, are not at high enough concentrations to combine significantly with the dihalomethylenes, the addition of iodide ions to the extent of several tenths molar can make such reactions important. The reactions possible for bromochloromethylene are analogous to those described in the previous section for chloroiodomethylene.

$$CBrCl + I^- \xrightarrow{k_2^{\mathrm{I}}} CBrClI^-$$

$$CBrCl + H_2O \xrightarrow{k_2^{\mathrm{W}}} H_2\overset{\oplus}{O}\text{-}\overset{\ominus}{C}ClBr \xrightarrow{\text{fast}} CO \text{ and } HCO_2^-$$

Thus iodide ion captures CBrCl to re-form CHBrClI and it captures CClI to produce $CHClI_2$. With the following definitions, H_0 = $[CHBrClI]_0$, x = $[CHBrClI]_0 - [CHBrClI]_t$, y = $[CHClI_2]_t$, B = $[OH^-]_t$, F_2 = fraction of the CBrCl's that react with water, the rate of reaction of CHBrClI may be expressed

$$\frac{dx}{dt} = \frac{k_1}{k_{-1}}(H_0 - x)(B)(k_2F_2 + k_3) \qquad (5)$$

With the analogous definition F_3 = fraction of the CClI's that react with water

$$\frac{dy}{dt} = \frac{k_1}{k_{-1}} k_3(1 - F_3)(H_0 - x)(B) - \frac{k_4}{k_{-4}} k_5F_3By \qquad (6)$$

Dividing (6) by (5) and inserting

$$F_2 = \frac{1}{1 + r_2[I^-]} \text{ and } F_3 = \frac{1}{1 + r_3[I^-]}$$

where $r_2 = k_2^{\mathrm{I}}/k_2^{\mathrm{W}}$, gives the relation

$$\frac{dy}{dx} = \frac{k_3r_3[I^-](1 + r_2[I^-])}{[k_2 + k_3(1 + r_2[I^-])](1 + r_3[I^-])} - \frac{(k_4k_5/k_{-4})(1 + r_2[I^-])}{(k_1/k_{-1})(k_2 + k_3 + k_3r_2[I^-])(1 + r_3[I^-])}\left(\frac{y}{H_0 - x}\right) \qquad (7)$$

Inserting the value of k_h^{Br} from eq. 3 and the analogous rate constant for the hydrolysis of chlorodiiodomethane

$$k_h^{\mathrm{CHClI_2}} = k_4k_5/k_{-4}$$

eq. 7 may be expressed as the linear differential equation

$$\frac{dy}{dx} = \frac{Ay}{H_0 - x} + Q \qquad (8)$$

where the constants A and Q are

$$A = \frac{-k_h^{\mathrm{CHClI_2}}(1 + r_2[I^-])}{k_h^{\mathrm{CHBrClI}}[1 + r_3[I^-] + f_1r_2[I^-](1 + r_3[I^-])]}$$

$$Q = \frac{r_3[I^-](1 + r_2[I^-])}{[r_2[I^-] + (1/f_1)](1 + r_3[I^-])}$$

f_1 being the fraction of the CHBrClI that reacts *via* loss of iodide ions

$$f_1 = k_3/(k_2 + k_3)$$

Eq. 8 may be solved by standard methods[7] to give

$$Q = \frac{(A + 1)(H_0 - x)^A y}{(H_0)^{A+1} - (H_0 - x)^{A+1}} \qquad (9)$$

Since only the rate constant ratio $k_h^{\mathrm{CHClI_2}}/k_h^{\mathrm{CHBrClI}}$, is needed (see the definition of A) in eq. 9, the fact that the available values of $k_h^{\mathrm{CHClI_2}}$ and k_h^{CHBrClI} (Table I) were determined in dilute solution does not prevent their use in the present case. The ionic strength effect on the basic hydrolysis of haloforms has been found to be quite small in those cases that have been studied[3,5] and should be very nearly the same for two such closely related compounds as those in question. It has also been found that r values do not change significantly with changing ionic strength and temperature,[3,5] so that the present value of r_3 determined at 64.5° (where more precise k's could be determined) and the previously reported[3] value of r_2 (7.31) should be useful. Values of x and y were determined by a method based on an infrared analysis of the CHBrClI and $CHClI_2$ content of the haloform mixture present in the reaction solution at

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

[7] *Cf.* A. L. Nelson, K. W. Folley and M. Coral, "Differential Equations," D. C. Heath and Co., New York, N. Y., 1952, p. 40.

any point. The total haloform concentration was calculated from the known initial bromochloroiodomethane concentration and the over-all *change* in haloform concentration, as revealed by the decrease in base concentration. The only unknown in eq. 9 is therefore f_I, which should be essentially independent of the ionic strength since k_2 and k_3 relate to such similar processes.

The infrared measurements permit two independent calculations of x and y for each point taken. For each such analysis a value of f_I was determined from eq. 9 by use of a high-speed computer. The results obtained are shown in Table II. Combination of the data in Table II with all the points (except two whose deviation was excessive) in two other runs with iodide concentrations up to 0.646 M gave an f_I value of 0.732 ± 0.019. The uncertainty is probably considerably larger than the average deviation because of possible errors in the k's and especially the r's used, and it may well be 10%.

TABLE II

THE HYDROLYSIS OF CHBrClI IN THE PRESENCE OF 0.388 M NaI AT 50°

Ml. HCl, 0.0500 M[a]	Optical density 8.505 μ 9.057 μ	8.615 μ 9.357 μ	[CHBrClI] Molarity	[CHClI$_2$] × 1000[b]	f_I
12.84	0.234	0.074	4.956	1.114	0.754
	.644	.157	4.906	1.164	.784
12.36	.199	.081	4.469	1.446	.732
	.553	.184	4.451	1.464	.740
11.91	.208	.105	4.028	1.742	.718
	.573	.247	4.028	1.742	.718
11.61	.232	.134	3.743	1.930	.708
	.637	.332	3.712	1.961	.720
11.34	.221	.149	3.430	2.156	.720
	.611	.379	3.417	2.169	.724
11.10	.248	.184	3.223	2.286	.710
	.665	.470	3.186	2.323	.722
10.81	.216	.177	3.000	2.415	.694
	.570	.460	2.943	2.472	.708
10.60	.257	.230	2.816	2.532	.690
	.679	.610	2.754	2.594	.706
10.50	.232	.225	2.666	2.649	.704
	.627	.617	2.608	2.707	.718
10.20	.234	.262	2.382	2.837	.704
	.621	.730	2.312	2.907	.722
				Av.	0.720 ± 0.014

[a] Per 50-ml. sample; initial titer 14.20 ml. [b] $[\mathrm{CHBrClI}]_0 = 6.509 \times 10^{-3}$ M, $[\mathrm{CHClI_2}]_0 = 0$.

The Correlation Equation.—From the f_I value determined it follows that the rate constant for the formation of chloroiodomethylene from bromochloroiodomethane and hydroxide ion at 50° is

$$k_1k_3/k_{-1} = f_I k_h^{\mathrm{CHBrClI}} = 4.05 \times 10^{-3}\ \mathrm{l.\ mole^{-1}\ sec.^{-1}}$$

and the rate constant for the formation of bromochloromethylene is

$$k_1k_2/k_{-1} = (1 - f_I)k_h^{\mathrm{CHBrClI}} = 1.48 \times 10^{-3}\ \mathrm{l.\ mole^{-1}\ sec.^{-1}}$$

These two rate constants may be treated by the correlation equation proposed previously[2] if we assume that the k_1 value for bromochloroiodomethane is equal to that for dibromochloromethane.[3] With this assumption, the methods used previously have been employed to calculate the values of log $(k_2/k_{-1})^{\mathrm{CX_2}}$ listed Exptl.

	Exptl.	Correl. eq.
log $(k_2/k_{-1})^{\mathrm{CBrCl}}$	4.847	4.722
log $(k_2/k_{-1})^{\mathrm{CClI}}$	4.409	4.491

These experimental values were used with the ten obtained previously to calculate the optimum parameters for the correlation equation by a least squares technique. The new values obtained (for 50°) are

$M_F = 3.071$
$M_{Cl} = 0.000$
$M_{Br} = -1.164$
$M_I = -1.696$
$N_{Br} = 1.090$
$N_I = 0.327$
$N_{Cl} = 0.000$
$c - d = 0.114$

These permit the calculation of the twelve log (k_2/k_{-1}) values (those for bromochloroiodomethane are given above) with an average deviation of 0.081, which we regard as a satisfactory fit even though the previous average deviation was 0.048.

Experimental and Calculations

Reagents.—The methods of preparation and purification of dibromochloromethane, dioxane, distilled water, standard sodium hydroxide and chlorodiiodomethane have been described previously.[2]

Bromochloroiodomethane.—A solution of 900 g. (6.0 moles) of sodium iodide and 255 ml. (3.0 moles) of dibromochloromethane in 1750 ml. of methanol was refluxed under nitrogen in the dark while 470 ml. of 4.8 M sodium methoxide was added dropwise over a period of four hours. When the solution had cooled, water was added until a heavy organic layer separated. This layer was washed with water and combined with two pentane extracts of the methanol-water layer. The organic layer was fractionally distilled, with 300 g. being collected between 61° and 71° at 24 mm. Refractionation yielded 200 g. (26%) of product, m.p. −24.5°; b.p., calcd. from an empirical equation,[8] 156.6°, found 68-69° (30 mm.) or 163° (extrapolated to 760 mm.); $n^{24.0}\mathrm{D}$ 1.6310, $d^{24.0}{}_4$ 2.802; molecular refractivity calcd. 32.250, found 32.391. Garino and Teofili report m.p. 5°, b.p. 180–190° with decomposition, density between 2.932 and 3.120.[4]

Hydrolysis Kinetics.—The alkaline hydrolysis of chlorodiiodomethane was studied by the previously described method B,[2] while method C[2] was used for bromochloroiodomethane. All reactions were carried out under nitrogen with the exclusion of light. In order to prevent free-radical reactions, 0.4% diphenylamine was added in the runs made in aqueous dioxane. This is more than an amount found sufficient to prevent radical reactions with iodoform,[2] a compound that should have a considerably larger tendency to undergo radical reactions. Rate constants were calculated from the integrated form of the appropriate second-order rate equation used previously.[2] The fraction of haloform that gives formate, f, was determined to be 0.10 ± 0.04 for bromochloroiodomethane in aqueous dioxane and this value also was used for the purely aqueous runs. An f value of zero was used for chlorodiiodomethane, as previously.[2] In order to test for the possibility of free-radical reactions during the hydrolysis of bromochloroiodomethane in pure water, runs were made in the presence of 0.4% p-phenylenediamine (diphenylamine is not soluble enough). While a strong red color was produced that obscured the phenolphthalein end-point, titrations using a pH meter gave rate constants within the experimental error of those obtained without an inhibitor.

Reaction of CHBrClI with Alkaline NaI Solution.—In a typical run, about 0.2 ml. of bromochloroiodomethane was measured from a "tuberculin" syringe calibrated in 0.01 ml. into 490 ml. of aqueous sodium iodide solution that was shaken vigorously until the haloform dissolved. A number of 50-ml. volumetric flasks were then filled with this solution to the 49-ml. marks that had been placed on them. The

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(8) J. Hine and S. J. Ehrenson, *J. Org. Chem.*, **21**, 819 (1956).

flasks were closed with rubber stoppers since the presence of stopcock grease may complicate the infrared analysis. To each flask was added 1.00 ml. of standard sodium hydroxide solution. At various times flasks were removed, cooled to 0° to stop the reaction, titrated to the phenolphthalein end-point and extracted with about 10 ml. of carbon disulfide. The extract was dried with silica gel, diluted if necessary and analyzed for bromochloroiodomethane and chlorodiiodomethane by infrared measurements.

To calculate f_I from eq. 9, initially, the magnitude of each side of the equation was determined for f_I values at small intervals over the entire range, 0.00 to 1.00, by use of an IBM model 650 data processing machine. After these calculations showed the approximate value of f_I, the range and the intervals were decreased in a recalculation.

Analysis of Haloform Mixtures.—The infrared analysis was carried out by the general method described previously.[3,9] The Beer–Lambert law was found to hold and the following extinction coefficients were determined at wave lengths of 8.505, 8.615, 9.057 and 9.357 μ, respectively; for bromochloroiodomethane, 59.4 ± 1.7, 5.97 ± 0.1, 173 ± 5 and 1.75 ± 0.03; for chlorodiiodomethane, 7.69 ± 0.16, 59.4 ± 1.5, 10.83 ± 0.37 and 173 ± 5. With measurements being made at four wave lengths it was possible to make two independent calculations of the composition of the haloform mixture. This was done and as shown in Table II there was good agreement between the two sets of values. Additional checks for artifacts due to other materials absorbing at the wave lengths used were made by extracting reaction solutions that had not had time to react appreciably and solutions containing no sodium iodide but in which considerable alkaline hydrolysis of bromochloroiodomethane had taken place. In each case the infrared analysis showed pure bromochloroiodomethane with no appreciable amount of chlorodiiodomethane. Extracts of reaction solutions from which bromochloroiodomethane had been omitted had no appreciable absorption at the wave lengths used for analysis. It was found that the extraction procedure used left practically no haloform in the aqueous solution, showing that preferential extraction of one of the two haloforms could not be affecting the results appreciably.

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[9] J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

A Study of *meta* Orientation in the Nitration of Toluene by Isotope Dilution Analysis[1]

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The proportion of *m*-nitrotoluene formed by mononitration of toluene with mixed acids at 0°, 30°, 45° and 60° has been determined using isotope dilution analysis.

The determination of isomer distribution among the products of mononitration of toluene has been the subject of a large number of studies. Only a few of the more careful and complete investigations are referred to here.[2–6] The proportion of *m*-nitrotoluene produced is of particular interest not only because of the theoretical implications but also because of its relationship to undesirable trinitrotoluene isomers which contaminate 2,4,6-trinitrotoluene (TNT). *m*-Nitrotoluene has been reported to be formed in amounts varying from 2.5 to 5.1% under widely different conditions of temperature and nitrating media. The methods of analysis used have been indirect and, in general, based upon comparison of unknown mixtures with mixtures of known isomers. These indirect methods have been necessary in the past because of the impossibility of making a quantitative separation of the small amount of *m*-isomer from its closely-similar *o*- and *p*-isomers. This problem is one to which the method of radioactive isotope dilution analysis is ideally suited.

For the nitration of radioactive toluene-1-C^{14} we chose a mixture of concentrated sulfuric and nitric acids, since this is by far the most commonly used nitrating medium. The nitrations were carried out on 2- to 5-gram batches of toluene, using slightly less than the stoichiometric amounts of nitric acid in order to minimize dinitration. Forty per cent. of the sulfuric acid was added to the toluene, vigorous stirring was begun, and the remainder of the sulfuric acid, mixed with the nitric acid, was added dropwise. This procedure avoided the production of appreciable heat of mixing during the addition and kept the toluene always in excess. After the length of time appropriate to reaction at temperatures of 0, 30, 45 and 60°, the reaction mixture was quenched with water and steam distilled. This allowed separation of the mixed nitrotoluenes from any unchanged toluene, dinitrotoluenes and oxidation products. A weighed sample of the mixed nitrotoluenes was diluted with a known amount of non-radioactive *m*-nitrotoluene and the mixture was distilled through an efficient micro-fractionating column in order to recover a pure sample of *m*-nitrotoluene. Known mixtures of *o*-, *m*- and *p*-nitrotoluene were previously distilled through the column to provide the experience and data necessary for successful fractionation. The *m*-nitrotoluene was oxidized by dichromate–sulfuric acid to *m*-nitrobenzoic acid and this material was radioassayed. The proportion of *m*-nitrotoluene present in the mixed nitrotoluenes was calculated from the usual inverse isotope dilution formula; *e.g.*,

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[1] Supported by U. S. Army Ordnance Research under Contract No. DA1-23-072-501-ORD-(P)-6. Taken in part from the Ph.D. thesis of Philip Heiberger, The University of Texas, 1953.

[2] A. F. Holleman, J. Vermeulen and W. J. de Moy, *Rec. trav. chim.*, **33**, 1 (1914).

[3] W. H. Gibson, R. Duckham and R. Fairbairn, *J. Chem. Soc.*, **121**, 270 (1922).

[4] C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, **130**, 1959 (1931).

[5] P. de Beule, *Bull. soc. chim. Belg.*, **42**, 27 (1933).

[6] W. W. Jones and M. Russell, *J. Chem. Soc.*, 921 (1947).