[CONTRIBUTION FROM DEFENCE RESEARCH CHEMICAL LABORATORIES, CANADA]

The Kinetics of the Alkaline Hydrolysis of 2-Nitriminoimidazolidine and 3-β-Aminoethylnitrourea at 25°[1]

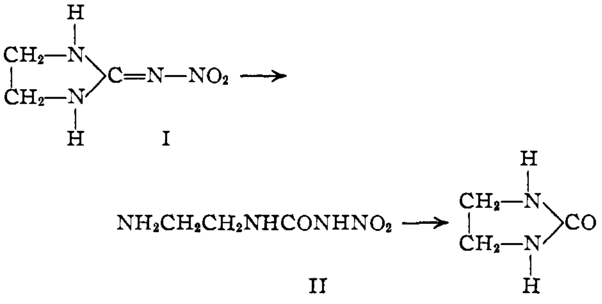
BY M. A. WEINBERGER AND A. F. MCKAY[2]

RECEIVED SEPTEMBER 16, 1954

The kinetics of the alkaline decomposition of 2-nitriminoimidazolidine (I) has been studied at 25°. The fast formation of the anion of I is followed by the hydration of the anion to give the anion IV of 3-β-aminoethylnitrourea. This in turn reacts with OH^- to give the final product. The hydration is subject to a small salt effect, whilst a large positive salt effect was found for the reaction of IV with OH^-.

There are many examples in the literature[3] of the alkaline hydrolysis at reflux temperatures of 2-nitriminoimidazolidines to the corresponding imidazolidones. The chemistry of alkaline hydration of 2-nitriminoimidazolidine (I) itself has been investigated by Wright and co-workers[4,5] and it was shown that at room temperature a compound could be isolated from the neutralized reaction mixture to which the structure 3-β-aminoethylnitrourea or 2-hydroxy-2-nitraminoimidazolidine was assigned. Kirkwood and Wright[5] concluded that it was impossible to distinguish between these structures on the basis of the chemistry of the hydration product. As will be shown, the ultraviolet absorption spectrum of the compound favors the structure 3-β-aminoethylnitrourea (II). The exact structure of this compound is, however, not important for the purpose of this paper and for convenience II will be used.

It thus appears that at room temperature the following reactions take place in alkaline solution



It is the purpose of the present work to investigate the kinetics of this sequence of reactions.

Experimental

The alkaline decompositions of 2-nitriminoimidazolidine and 3-β-aminoethylnitrourea at 25° were followed by observing the decrease in the absorption of the two compounds at 255 mμ, using a Beckman DU spectrophotometer. The reactions were carried out in a thermostated absorption cell somewhat similar but of improved design to that used by Willi and Robertson.[6] The reaction mixture was continuously circulated through the absorption cell by a centrifugal pump stirrer. The cell was mounted in a carriage fitted with rails which moved in grooves cut into end plates. The whole assembly was fixed to the spectrophotometer instead of the usual cell holder and mount. The carriage also held a reference cell and it could be moved relative to the end plates by a wheel turned screw thus placing either the reference cell or the reaction cell into the light beam. A glass sealed thermistor (Western Electric #14B) served to measure the temperature inside the reaction vessel. It was connected in a conventional Wheatstone Bridge circuit and the out-of-balance current amplified and recorded. Temperature fluctuations during a run were held within ±0.03°. For runs taking longer than a day the absorption readings were taken in the normal way by withdrawing aliquots from the reaction mixture contained in tubes immersed in a thermostat.

2-Nitriminoimidazolidine.—This was prepared as previously described.[7] It melted at 220.5–221° dec. after three recrystallizations from water.

3-β-Aminoethylnitrourea.[4]—Six grams (0.046 mole) of 2-nitriminoimidazolidine was dissolved in 500 cc. of 0.2 *N* NaOH. After standing for 24 hr. at room temperature, the solution was neutralized with concd. HCl and evaporated to dryness *in vacuo* under nitrogen. The material was extracted with boiling acetone (2 × 100 cc.) to dissolve any 2-nitriminoimidazolidine. The residue was taken up in 16 cc. of H_2O and the solution cooled. On standing overnight colorless crystals precipitated which were filtered and washed with ice-water, m.p. 135.5–137° dec., 2.38 g. (37%). Recrystallization from hot water gave a sample with a constant melting point of 139° dec.

Results and Discussion

The ultraviolet absorption spectra of II in aqueous and alkaline solutions are shown in Fig. 1. The spectrum in aqueous solution is typical of that of a nitrourea and not that of a simple nitramine. Following the arguments of McKay and Sandorfy,[8] the linear structure II should be assigned to the hydration product of 2-nitriminoimidazolidine.

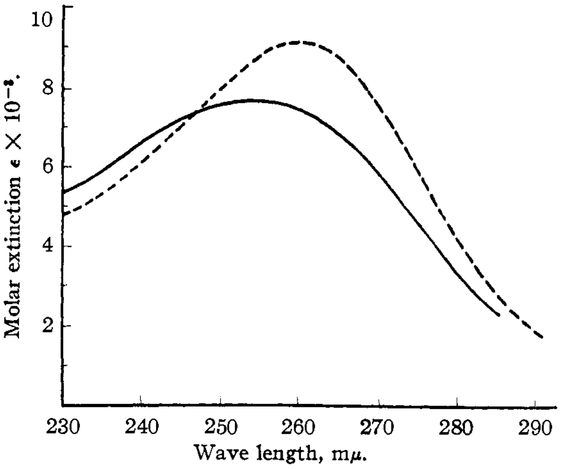


Fig. 1.—Absorption spectra of 3-β-aminoethylnitrourea: ---, in aqueous solution; —, in 0.5 *N* NaOH.

The spectra of I in aqueous and alkaline solutions have been described.[9]

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[1] Issued as DRCL Report No. 104.

[2] Monsanto (Canada) Ltd., LaSalle, Quebec.

[3] A. F. McKay, *Chem. Revs.*, **51**, 301 (1952).

[4] S. S. Barton, R. H. Hall and G. F. Wright, THIS JOURNAL, **73**, 2201 (1951).

[5] M. W. Kirkwood and G. F. Wright, *ibid.*, **76**, 1836 (1954).

[6] A. V. Willi and R. E. Robertson, *Can. J. Chem.*, **31**, 361 (1953).

[7] A. F. McKay and G. F. Wright, THIS JOURNAL, **70**, 430 (1948).

[8] A. F. McKay and C. Sandorfy, *Can. J. Chem.*, **31**, 42 (1953).

[9] A. F. McKay, J. P. Picard and P. E. Brunet, *ibid.*, **29**, 746 (1951).

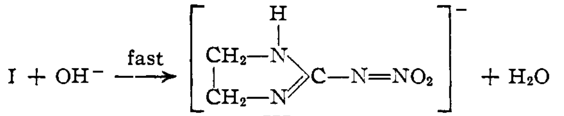
Experiments were carried out to study the effect of sodium hydroxide concentration on the absorption spectra of I and II. The alkali concentration was varied from 0.2 to 2 *N* and in all cases the absorption curves were identical. Furthermore, it was found that there was an immediate shift from the aqueous to the alkaline absorption spectrum on adding the aqueous solutions of I and II to alkali, irrespective of the concentration of the latter. This indicates that in alkaline solution the species responsible for absorption are formed by a fast reaction and that further no equilibrium is involved. These species are presumably the anions of 2-nitriminoimidazolidine (III) and 3-β-aminoethylnitrourea (IV).

These findings are in agreement with those of de Vries and Gantz[10] but at variance with the potentiometric titration data of Barton, Hall and Wright.[4] This discrepancy already has been discussed by the authors.[11]

The validity of Beer's law at 255 mμ for alkaline solutions of I and II is illustrated in Fig. 2. The molar extinction coefficients ε were found to be

$$\left.\begin{array}{l}\epsilon_{III} = 8.81 \times 10^3 \\ \epsilon_{IV} = 7.84 \times 10^3\end{array}\right\} \text{at } 255 \text{ m}\mu$$

These are independent of alkali concentration. The first step in the alkaline hydration of I is thus the non-rate determining reaction



III

This is followed by the formation of

$[NH_2CH_2CH_2NHCONNO_2]^-$ IV

which subsequently decomposes. As both III and IV absorb to almost the same extent at 255 mμ, the kinetics of the decomposition of IV have to be known before those of the reaction III → IV can be deduced.

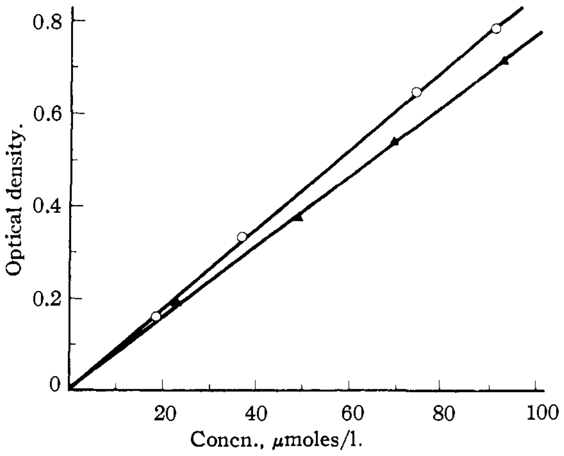


Fig. 2.—Beer's law at 255 mμ for reactants: O—O, 2-nitriminoimidazolidine in 0.8 *N* NaOH; ▲—▲, 3-β-aminoethylnitrourea in 0.5 *N* NaOH.

The Kinetics of Hydrolysis of 3-β-Aminoethylnitrourea.—The hydrolyses were carried out in 0.25 to 2 *N* sodium hydroxide, the solutions being about 0.0004 *M* in II. The alkali was therefore in large excess and any fluctuation in its concentration due to participation in the reaction may be neglected. The final product had no absorption at 255 mμ so that the optical density *E* is a measure of the concentration of IV at any time.

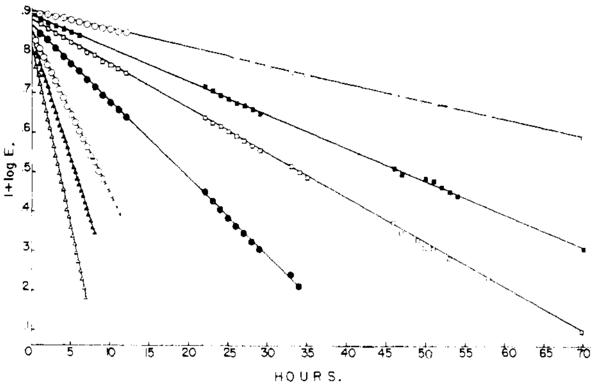


Fig. 3.—Plots of log *E* *vs.* time for decomposition of 3-β-aminoethylnitrourea at various alkali concentrations: ⊙—⊙, 0.249 *N* NaOH; ■—■, 0.390 *N* NaOH; □—□, 0.490 *N* NaOH; ●—●, 0.718 *N* NaOH; O—O, 1.189 *N* NaOH; ▲—▲, 1.529 *N* NaOH; △—△, 1.901 *N* NaOH.

The plots of log *E* *vs.* time for the various alkali concentrations are shown in Fig. 3. All are excellent straight lines. The velocity constants were calculated using the generalized method of least squares[12] and are shown in Table I together with the standard errors which indicate the goodness of fit of the simple exponential law $E = E_0e^{-k_2't}$

Table I

NaOH, *N*	Pseudo 1st-order constants k_2', hr.$^{-1}$	k_2, l. mole^{-1} hr.$^{-1}$
0.249	0.0105 ± 0.00003	0.0426
.390	.0193	.0495
.490	.0261 ± .00004	.0533
.718	.0445 ± .0001	.0620
1.189	.0956 ± .0002	.0804
1.529	.1426 ± .0003	.0932
1.901	.2077 ± .0004	.1092

The third column of the table gives the values of k_2 for the reaction

$$IV + OH^- \xrightarrow{k_2} \text{products (non-absorbing)}$$

and were obtained by dividing the pseudo first order constants k_2' by the respective $[OH^-]$.

As can be seen, k_2 increases with increasing $[OH^-]$. This is to be expected, since there will be a positive salt effect for a reaction between ions of the same sign.

In attempting to deal with this salt effect quantitatively one is, of course, faced with the difficulty that the solutions are far too concentrated in alkali for the simple Debye–Hückel expressions to hold.

It was therefore tried to fit an expression which is

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(10) J. E. de Vries and E. St. C. Gantz, This Journal, **76**, 1008 (1954).

(11) A. F. McKay, M. A. Weinberger, *et al.*, *ibid.*, **76**, 6371 (1954).

(12) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

known to hold for more concentrated solutions.[13] This is

$$\log_{10} k_2 = \log k_2^\circ + \frac{2A\sqrt{\mu}}{B\sqrt{\mu} + 1} + C\mu$$

Here k_2° is the velocity constant at zero ionic strength μ which was taken as $[OH^-]$. At 25° $A = 0.509$ in aqueous solution. Values of k_2°, B and C were calculated from the experimental values of k_2 by the generalized method of least squares.[12] The values obtained were: $k_2^\circ = 0.01930$ mole^{-1} l. hr.$^{-1}$; $B = 1.2553$ mole$^{-1/2}$; $C = 0.1257$ mole^{-1}. Whilst because of the high concentrations involved, the authors do not claim more than an empirical significance for the expression for the salt effect, it is interesting to see that the value of B is of the right order of magnitude when compared with that used in other connections.[14] The authors are therefore confident that the variation of k_2 with alkali concentration is due to a primary salt effect alone.

A plot of $\log_{10}k_2$ *vs.* $2A\sqrt{\mu}/B\sqrt{\mu} + 1 + C\mu$, using the above values of A, B and C is shown in Fig. 4. The slope of the line is 1.00.

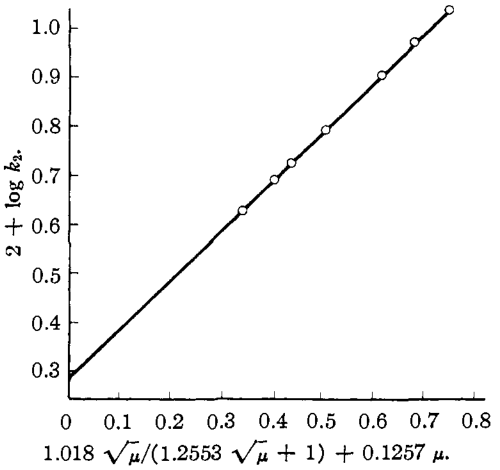

Fig. 4.—Salt effect on k_2.

The Kinetics of Hydration of 2-Nitrimino-imidazolidine.—As there is only a small change in light absorption when I is hydrated to give II and the process is further complicated by subsequent decomposition of II it was impracticable to study the conversion directly. Runs were therefore carried out using similar concentrations of alkali and I, as in the case of II. From the known value of k_2 or k_2', the value of a pseudo first-order constant k_1' could be calculated at the various alkali concentrations for the reaction

$$\text{III} \xrightarrow[k_1']{H_2O,\ OH^-} \text{IV}$$

If x is the concentration of III, y the concentration of IV, E_t the optical density at time t in a 1-cm. cell and the ϵ's the extinction coefficients, then the rate equations are

$$-\,dx/dt = k_1'x$$
$$dy/dt = k_1'x - k_2'y$$
$$E_t = \epsilon_{III}x + \epsilon_{IV}y$$
$$E_0 = \epsilon_{III}x_0$$

Solution of these equations yields

$$\frac{E_t}{E_0} = \left(1 + \frac{\eta k_1'}{k_2' - k_1'}\right)e^{-k_1't} - \frac{\eta k_1'}{k_2' - k_1'}\,e^{-k_2't}$$

where

$$\eta = \epsilon_{IV}/\epsilon_{III} = 0.890$$

For purposes of calculation, the form

$$E_t/E_0 = \left(1 + \frac{\eta\lambda}{1 - \lambda}\right)e^{-k_2't} - \frac{\eta\lambda}{1 - \lambda}\,e^{-k_2't}$$

was used where $\lambda = k_1'/k_2'$.

λ for each alkali concentration was calculated using the method of least squares.[12] As this method in its generalized form only utilizes the first term of a Taylor series, a number of successive approximations were necessary. The calculations were somewhat laborious, as there were about 20–30 points in each experiment. The calculated values of k_1' with their standard errors are shown in Table II and the curves of E_t/E_0 *vs.* t calculated with these values and those of k_2' are plotted in Fig. 5, together with the experimentally observed values of E_t/E_0.

TABLE II

NaOH, *N*	k_1', hr.$^{-1}$
0.718	0.1309 ± 0.0006
1.186	.1363 ± .0002
1.532	.1387 ± .0012
1.920	.1461 ± .0005

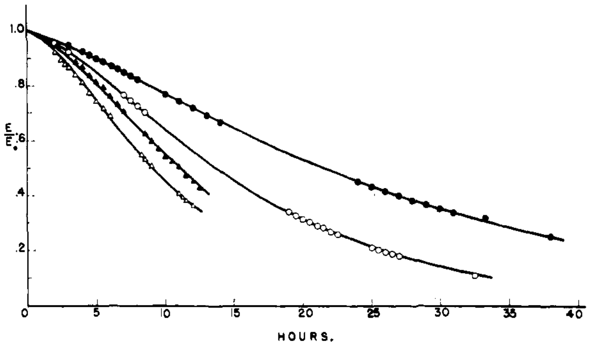

Fig. 5.—Plots of E/E_0 *vs.* time for reaction of 2-nitrimino-imidazolidine with alkali. The curves are calculated. The points are experimental values: ●, 0.718 *N* NaOH; ○, 1.186 *N* NaOH; ▲, 1.532 *N* NaOH; △, 1.920 *N* NaOH.

It was found that owing to the indirect method of calculating k_1' the error in k_1' due to an error in k_2 increased very rapidly with decreasing alkali concentration at values lower than 0.7 *N*. Values of k_1' obtained from runs at these lower concentrations are therefore not reliable and are not quoted.

As can be seen from Table II, k_1', unlike k_2', is essentially independent of alkali concentration, apart from a slight salt effect to be expected at these high concentrations for a reaction between an ion and a neutral molecule.[13] This salt effect is proportional to the ionic strength (taken as alkali concentration) and is illustrated in Fig. 6. The actual variation of k_1' with ionic strength is given by

$$k_1' = 0.1218 + 0.01213\mu$$
$$(\text{hr.}^{-1})$$

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[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 138–140.

[14] Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, N. Y., 1946, p. 146.

The reaction III → IV is thus

$$\text{III} + H_2O \xrightarrow{k_1} \text{IV}$$

and does not involve OH^-. As the other reactant is water, it is sufficient to quote the pseudo first-order constant k_1'.

The observed kinetics can thus be explained by the following mechanism for the decomposition of 2-nitriminoimidazolidine in alkali solutions.

$$\text{I} + OH^- \xrightarrow{\text{fast}} \text{III}$$

$$\text{III} + H_2O \xrightarrow{k_1} \text{IV}$$

$$\text{IV} + OH^- \xrightarrow{k_2} \text{2-imidazolidone}$$

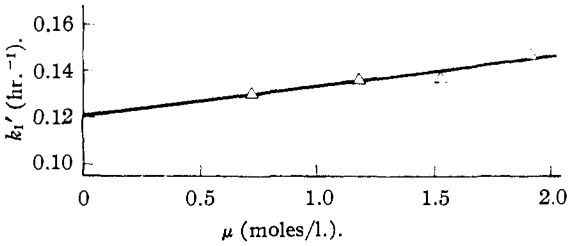

Fig. 6.—Salt effect on k_1'.

Acknowledgments.—The authors would like to thank Mr. G. Ensell, National Research Council, for construction of the absorption cell; Mr. W. G. Hatton of these Laboratories for the preparation of the reactants and Mr. D. Irwin for help with the experiments and calculations. Thanks are also due to Dr. E. Whalley and Dr. R. E. Robertson of the National Research Council for helpful discussions.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Chemistry of Nitrite Ion in Aqueous Solution[1]

BY HAROLD A. SCHWARZ AND AUGUSTINE O. ALLEN

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When deaerated solutions of KNO_2 at their natural *p*H are irradiated with γ- or X-rays, the main initial reaction is a formation of hydrogen and hydrogen peroxide. As peroxide builds up, a radiation-induced reaction between nitrite and peroxide sets in, which results in the formation of nitrate. This reaction is slower the higher the nitrite concentration. The kinetics of the nitrite–peroxide reaction were studied in detail by the irradiation of synthetic mixtures, and the results were satisfactorily explained by a free radical mechanism. The main feature of the mechanism is a competition between H_2O_2 and NO_2^- for reaction with H atoms generated in the water. The yield for H-atom formation is found to be 2.4 per 100 e.v. The initial yield of peroxide in the pure nitrite solutions is greater than the yield of hydrogen, and decreases with increasing nitrite concentration, at concentrations below 0.002 *M*. The effect of nitrite on the initial peroxide yield is qualitatively similar to the effect of bromide reported by Sworski. In nitrite solutions containing oxygen, an immediate nitrite oxidation occurs on irradiation, with a yield which increases with increasing ratio of the concentration of nitrite to that of oxygen.

The effect of X-rays on dilute aqueous solutions of KNO_2 has been briefly investigated by Fricke and Hart[2] and by Lefort.[3] A more extensive investigation was made in the hope that it might give some information as to the relative importance of the various modes of decomposition of water when subjected to ionizing radiations.

Experimental

Baker and Adamson reagent grade KNO_2 was recrystallized six times from water, thereby reducing the nitrate impurity to 0.6 mole %. This method of purification is difficult because the solubility of KNO_2 is high and has a small temperature coefficient. Reagent grade material gave the same results as the recrystallized KNO_2, and was used without further purification in later work. J. T. Baker C.P. 30% hydrogen peroxide was used without further purification. Distilled water was further purified as described by Johnson and Allen.[4] All other reagents were reagent grade and not further purified.

Three radiation sources were used. X-Rays were obtained by bombarding a gold target with 2 Mev. electrons from a Van de Graaff generator made by the High Voltage Engineering Corporation of Cambridge, Massachusetts. Two hollow cylindrical Co^{60} sources, of 120- and 1500-curie strength, supplied γ-rays. The dose rates[5] employed, in terms of μmole/l. min. of $FeSO_4$ oxidized in aerated 0.4 *M* H_2SO_4, were 42.5 for the X-rays, 12.0 and 143 for the γ-rays. During irradiation, the sample temperatures were close to 25° in all cases.

The deaerated samples were prepared by a procedure similar to that used by Johnson.[4] The cells used with the Van de Graaff generator were flat cylinders about 40 mm. in diameter and 20 mm. long, with the filling arm coming off one edge. The cells used with the cobalt source were tubes 10 mm. i.d. and 15 cm. long.

Nitrate was determined by the phenoldisulfonic acid method given by Snell.[6] Nitrite interferes with the analysis and was removed before evaporation and addition of the reagent solution by reaction with sulfamic acid. A 15-cc. portion of solution was taken; the final solution was made to 50 cc. and the optical density read on a Beckman model DU spectrophotometer. (One centimeter cells were used for all spectrophotometric work.) At 400 mμ, nitrate concn. (μ *M*) = 510 × O.D. This method did not give very satisfactory analyses, the probable error being of the order of 10%.

Hydrogen peroxide was determined by the method of J. A. Ghormley.[7,8] A standardization of the method (diluting the sample two to five) at 350 mμ gave: concn. (μ*M*) = 97.3 × O.D., which is in good agreement with the value given by Hochanadel.[8] Nitrite oxidizes iodide, and might be expected to interfere with the analysis. The reaction

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 365 (1935).

[3] M. Lefort, Thesis, University of Paris, 1950.

[4] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[5] In conformity with common usage in the field of radiation chemistry of aqueous solutions, the word "dose" is used in this paper to mean the total energy input, due to the irradiation, per unit volume of irradiated material. This usage is not strictly in accord with the more generally accepted meaning, which is the total energy input per unit mass of material (L. D. Marinelli, *Ann. Rev. Nuclear Sci.*, **3**, 249 (1953)).

[6] F. D. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 269.

[7] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

[8] C. J. Hochanadel, *ibid.*, **56**, 587 (1952).