substance by the following sequence of reactions: oxidation with Br_2/OH^- [11b] to the corresponding acid, reduction to the alcohol with $LiAlH_4$,[11c] and subsequent oxidation to the aldehyde with ceric ammonium nitrate.[11d]
(11) (a) R. Adams and L. R. Noller, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 109; (b) R. Levine and J. R. Stephens, *J. Am. Chem.*, **72**, 1642 (1950); (c) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947); (d) W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965).
(12) This sample has been prepared by Rosenmund reduction of *p*-chlorobenzoyl chloride by deuterium gas, cf. A. F. Thomson and H. H. Cromwell, *J. Am. Chem. Soc.*, **61**, 1374 (1939).
(13) O. S. Khalil and L. Goodman, *J. Phys. Chem.*, **80**, 2170 (1976).
(14) O. S. Khalil and L. Goodman, *J. Chem. Phys.*, **65**, 4061 (1976).
(15) S. W. Hankin, O. S. Khalil, and L. Goodman, preparation for publication.
(16) H. G. Silver and J. L. Woods, *Trans Faraday Soc.*, **60**, 5 (1964).
(17) M. Koyanagi, R. M. Zwarich, and L. Goodman, *J. Chem. Phys.*, **56**, 3044 (1972).
(18) N. Kanamaru, M. E. Long, and E. C. Lim, *Chem. Phys. Lett.*, **26**, 1 (1974).
(19) H. J. Pownall and J. R. Huber, *J. Am. Chem. Soc.*, **93**, 6429 (1971).
(20) H. J. Pownall, R. E. Connors, and J. R. Huber, *Chem. Phys. Lett.*, **22**, 403 (1973).
(21) H. J. Pownall and W. W. Mantulin, *Mol. Phys.*, **31**, 1393 (1976).
(22) S. Y. Chu and L. Goodman, *J. Mol. Spectrosc.*, submitted for publication.
(23) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).
(24) F. B. Tudron, J. M. Van Pruyssen, and S. D. Colson, *J. Chem. Phys.*, **63**, 2086 (1975).
(25) J. M. Van Pruyssen and S. D. Colson, *Chem. Phys.*, **6**, 382 (1974).
(26) J. W. Robinson and P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **36**, 1187 (1963).
(27) A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960).
(28) P. M. Johnson and L. Ziegler, *J. Chem. Phys.*, **56**, 2169 (1972).
(29) G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, **15**, 465 (1972).
(30) G. Orlandi and W. Siebrand, *J. Chem. Phys.*, **58**, 4513 (1973).
(31) S. F. Fischer and E. C. Lim, *Chem. Phys. Lett.*, **14**, 40 (1972).
(32) E. W. Schlag, S. Schneider, and S. F. Fischer, *Annu. Rev. Phys. Chem.*, **22**, 465 (1971).
(33) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).
(34) J. B. Birks, "Organic Molecular Photophysics", Vol. 2, Wiley, New York, N.Y., 1975, Chapter 9, and references therein.
(35) M. Long and E. Lim, *Chem. Phys. Lett.*, **20**, 413 (1973).
(36) L. Hall and M. A. El-Sayed, *Chem. Phys.*, **8**, 272 (1975).

Radiation Chemistry of Aqueous Cyanide Ion[1]

B. H. J. Bielski* and Augustine O. Allen

Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. *Received January 28, 1977*

Abstract: Dilute KCN solutions, irradiated with γ rays in the presence of N_2O, give radicals $CONH_2$ which react quantitatively by disproportionation to yield equal amounts of cyanate and formamide. In the absence of N_2O, the radicals $CONH_2$ and H_2CN are formed and interact to yield a more complicated spectrum of products.

Exposure of aqueous solutions to high-energy radiations results in attack on solutes by hydrated electrons and radicals OH and H. The radiation chemistry of the solute consists of a resulting series of reactions. The radiation chemistry of cyanide solutions is of interest because of the relationship of cyanide to the halides, the radiation chemistry of which has been much studied, and because of its possible role in prebiological chemical evolution on the primitive earth. Photochemical or thermal treatment of cyanide solutions has been found to yield adenine and other interesting compounds.[2,3] Since far-ultraviolet light, penetrating the primitive oxygen-free atmosphere, could produce hydrated electrons and OH radicals in the surface layer of the oceans, study of the radiation chemistry of cyanide might also be relevant.

Recent pulse-radiolysis studies[4,5] have established the nature of the initially formed radicals in HCN and CN^- solutions. Some data on yields of the final products, especially from acid solutions, are reported by Ogura et al.[6,7] The present work reports detailed product analyses from irradiation of cyanide solutions at pH 11, with and without addition of N_2O to convert solvated electrons to OH radicals.

Experimental Section

Irradiations. Most of the work employed ^{60}Co γ rays; two sources were used, with intensities differing by a factor of 7. Pulse radiolysis was carried out as previously described.[8] All irradiations and analyses (except as noted) were made at room temperature (~22 °C).

Materials. Baker Analyzed Reagent KCN was recrystallized. Solutions were made in triple-distilled water saturated with N_2, Ar, or N_2O after boiling to expel CO_2 and O_2. $K^{14}CN$ from Schwarz Bio Research Inc. was treated with barium salt to remove carbonate, then purified by distillation from an acid solution to an alkaline one in a Conway diffusion apparatus.[9] Other labeled compounds (for testing product identifications and behavior) were obtained from ICN Tracerlab.

Analytical Methods. Hydrogen and nitrogen gases were determined by chromatography as described elsewhere.[10] Hydrogen peroxide was determined by adding ceric sulfate to the solution and determining the resulting oxygen by gas chromatography along with the nitrogen. Carbonate was determined by a modification of Carpenter's method.[11] The solution was acidified and warmed to 48 °C for 20 min, then the evolved gas passed into a Varian Aerograph gas chromatograph. Evolution of CO_2 was, however, not quantitative at low concentrations and the method had to be calibrated with known solutions.

Cyanide was determined as the Ni complex[12] or by the chloramine-T method;[13] good agreement was found between the two methods.

Ammonia was determined by the Orion ammonia electrode, Model 95-10.[14]

Formamide was determined as formate after base hydrolysis, using the quinaldinium iodide method.[15] The difference between the NH_3 content before and after hydrolysis provided a check on the result.

Cyanate was determined by the amounts of CO_2 and ammonia formed in acid hydrolysis of irradiated solutions. Its appearance in considerable yields was verified by paper chromatography, but this did not provide a quantitative determination, since some decomposition occurred in the acidic chromatographic solution.

Formaldehyde was determined by the acetylacetone method.[16]

Nonvolatile products were determined by descending paper chromatography of irradiated $K^{14}CN$ solution on Whatman no. 1 filter paper with 1-butanol-acetic acid-water (4:1:5) developer. As the solution migrates down the paper, components are held back in strips occurring at different fractions R_f of the total distance to the solvent front. Positions of the strips were found by placing the paper on an x-ray plate. R_f values for numerous compounds are tabulated[17] for this particular solvent. For further identification, the paper was cut into strips and tested with various reagents. After tentative identification, authentic samples of the compounds were run for comparison. The compounds found and their R_f values are listed in Table I. For quantitative determination, strips were cut out and completely eluted with water and the ^{14}C was counted in Aquasol (New England Nuclear) on a Beckman liquid scintillation system.

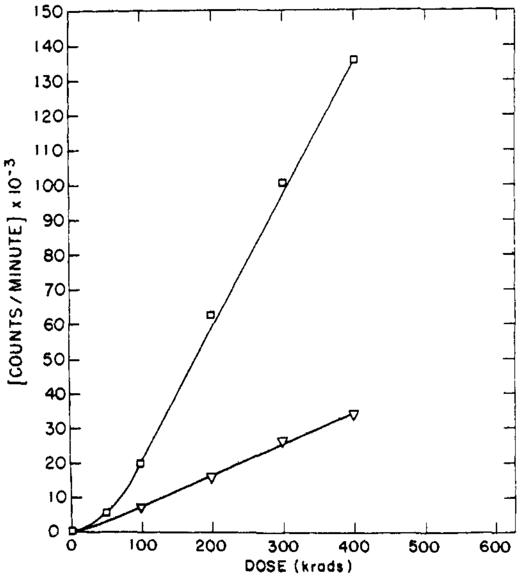

Figure 1. Radiation induced formation of glycine (□) and urea (▽) in N_2 saturated 5 mM KCN containing $K^{14}CN$. Dose: 10^3 counts are equal to 0.107 G per ^{14}C atom; 10 krad/min.

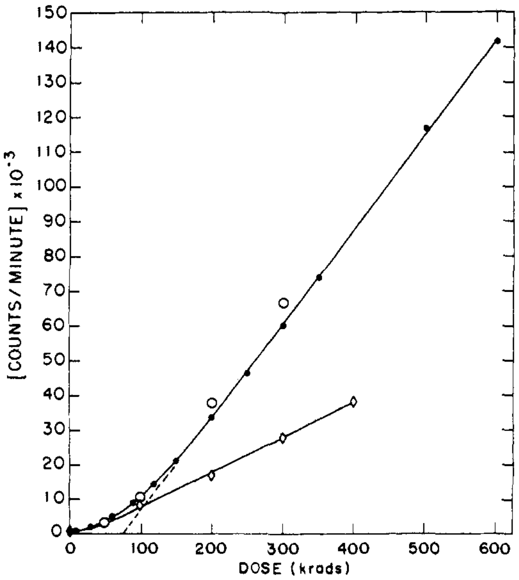

Figure 2. Radiation induced formation of unknown with $R_f = 0.20$ (○, ●) and $R_f = 0.25$ (◇). The symbols ○ and ◇ show the formation of unknowns in N_2 saturated 5 mM KCN solution containing $K^{14}CN$. The symbol ● represents equivalent optical absorbance changes at 248 nm for the unknown with $R_f = 0.20$. Dose: 10^3 counts are equal to 0.106 G per ^{14}C atom; 10 krad/min.

Results

Irradiations under N_2O. The results shown in Table II comprise a great number of runs, each run consisting of at least five determinations made at different doses. The yields found in these solutions by paper chromatography were all extremely small, with the exception of cyanate, and are omitted from the table. Cyanate yield appearing in the paper is in rough agreement with the value found from acid hydrolysis to CO_2 and ammonia. The formate and ammonia found after basic hydrolysis are equal, and practically the same as the CO_2 and ammonia found after acid hydrolysis. The nitrogen yield has the value expected[8] from the reaction of solvated electron with N_2O

$$H_2O + e^-_{aq} + N_2O = N_2 + OH + OH^- \quad (1)$$

Table I. Products Found by Paper Chromatography in Radiolyzed 0.005 M KCN Solutions, Developed by 1-Butanol-Acetic Acid-Water (4:1:5)

Compd	R_f
Cyanamide	0.66 ± 0.02
Urea	0.53 ± 0.03
Cyanate	0.44 ± 0.02
Glycine[a]	0.36 ± 0.02
	0.28 ± 0.02
Unknown	0.25 ± 0.01
Unknown (peak at 250 nm)	0.20 ± 0.01
Formic acid	0.16 ± 0.01
"Polymer"	0.00

[a] Two bands arise from the neutral and the zwitterion forms of the compound.

Table II. Product Yields from Irradiation of 0.005 M KCN Solutions, pH 11.0, Saturated with N_2O

Compd	G^a	Method
Cyanide, CN^-	−6.2 ± 0.4	Ni complex and chloramine-T
Nitrogen, N_2	3.05 ± 0.05	Gas chromatography
Cyanate, CNO^-	3.3 ± 0.4	As CO_2 after acid treatment, by gas chromatography
Formamide, $HCONH_2$	3.4 ± 0.1	As formate after alkaline hydrolysis, by quinaldinium iodide
Ammonia, NH_3:		Ammonia electrode
After acid hydrolysis	3.3 ± 0.2	
After alkaline hydrolysis	3.4 ± 0.2	
After acid, followed by alkaline drolysis	6.5 ± 0.3	
Hydrogen peroxide, H_2O_2	0.71 ± 0.06	As O_2, after $Ce(SO_4)_2$ addition, by gas chromatography
Hydrogen, H_2	0.42 ± 0.01	Gas chromatography
Formaldehyde, H_2CO	0.02 ± 0.01	Acetylacetone method

[a] Molecules formed per 100 eV of γ-ray energy absorbed by the olution.

The yields found for H_2O_2 and H_2 were those arising directly from radiolysis of water;[18] the N_2O and cyanide protect them from radical attack.

Thus cyanate and formamide, produced in equal amounts, are the only products of any importance resulting from the action of OH radicals on cyanide ions.

Pulse Radiolysis Studies. The rate of reaction of OH with CN^- was found by competition with $Fe(CN)_6^{4-}$ to be $(8 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$, in good agreement with published values.[4,5] The lifetime of the solvated electron in our triple-distilled water (22 μs) was not changed by small concentrations of KCN. In 0.125 and 0.25 M KCN, shortening of the lifetime occurred, which corresponded to a reaction rate constant with KCN of 3×10^5. The effect could have arisen from as little as 0.002% of a reactive impurity in the KCN; for all practical purposes, the cyanide ion does not react with solvated electrons.

Reactions in Nitrogen-Saturated Solutions. With solvated electrons and OH radicals both present, the product spectrum became more complicated. Figures 1-3 show the growth of concentration with increasing γ-ray dose for five products which were determined by paper chromatography and formamide. Four of these show definite induction periods. The yield values, G, shown in Table III for these compounds are calculated from the linear rates of growth found after the induction

Table III. Product Yields from γ Irradiation of 0.005 M KCN Solutions Saturated with Nitrogen

Compd	G^a	Remarks
Cyanide, CN^-	−2.91 ± 0.15	
Cyanate, CNO^-	0.65 ± 0.07	CO_2 yield after acid hydrolysis. Elution from paper gave 0.60
Ammonia, NH_3	1.13^b ± 0.13	After acid and base hydrolysis
Formamide	0.83 ± 0.06	Quinaldinium iodide method
Formaldehyde, H_2CO	0.02 ± 0.01	
Hydrogen, H_2	0.45 ± 0.01	
Cyanamide, $CNNH_2$	0.01 ± 0.005	
Urea, $CO(NH_2)_2$	0.10 ± 0.02	
Glycine, H_2NCH_2COOH	$0.43^{c,d}$ ± 0.02	
Unknown, R_f 0.25	0.11^c ± 0.01	
Unknown, R_f 0.20	0.29^c ± 0.02	

[a] For products showing an induction period, G is calculated from the rate of increase of concentration with dose after the induction period. [b] This determination is probably in error; it should be at least equal to the sum of cyanate and formamide $G \sim 1.48$, since both yield ammonia upon acid and base hydrolysis, respectively. The observed low value $G = 1.13$ suggests that cyanate and/or formamide most likely undergo acid and/or base catalyzed reaction(s) with radiation generated product(s). [c] Number of C atoms formed in the compound per 100 eV absorbed by the cyanide solution. [d] Sum of two bands.

period. Other yields were independent of dose, except that of cyanate, which decreased slightly at the higher doses.

Radiograms of the paper showed that the insoluble "polymer" which did not migrate on the paper formed with higher yield in N_2-saturated than in N_2O-saturated solutions. It was impossible to elute this material from the paper, so no quantitative determination of it was made.

Tests for methanol and for CO or other volatile products which could appear in a gas chromatogram, also for hydrazine and hydroxylamine, were negative.

Spectrophotometry of irradiated solutions showed the growth of a symmetrical absorption band having a peak at 248 nm, reported also by Ogura et al.[7] Spectroscopic examination of the eluted fractions showed this absorption band was due to the unknown compound with $R_f = 0.20$. The band disappeared when the solution was acidified and reappeared reversibly when base was added. A symmetrical titration curve of optical density vs. pH was obtained, giving $pK_a = 8.8$. The compound reacts with ninhydrin and is presumably an amine.

Literature surveys and comparison tests with different compounds failed to identify either the $R_f = 0.20$ or the $R_f = 0.25$ product. Among the compounds tried were three obtained from spontaneous polymerization of more concentrated cyanide solutions, kindly sent to us by E. Sanchez of the Salk Institute: diaminomaleonitrile, 4-amino-5-cyanoimidazole (AICN) and its hydrolysis product. The AICN proved to have an optical absorption band peaking at 247 nm resembling very closely the absorption spectrum of our unknown, but the R_f values found in our procedure were very different: 0.77 for AICN, 0.20 for the unknown. The close resemblance of the spectra suggests that this unknown may be an isomer of AICN. We found no clues to the identity of the other unknown product.

The carbon atoms found in the products listed in Table III add up to a G of only 2.44, although the cyanide disappears with $G = 2.91$. The balance, 0.47, presumably is in the insoluble "polymer".

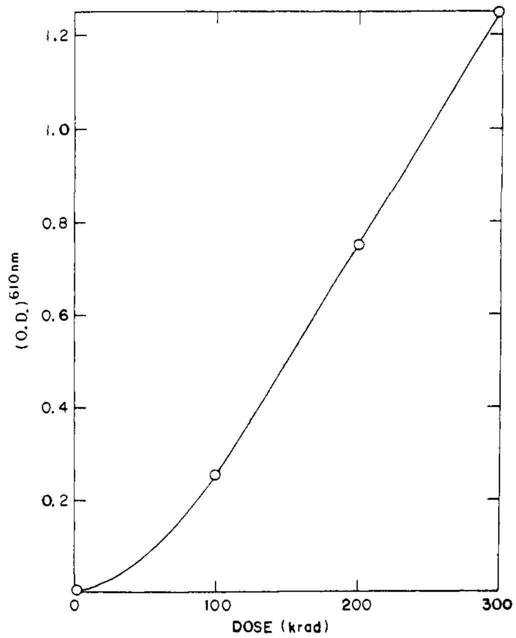

Figure 3. Radiation induced formation of formamide in N_2 saturated 5 mM KCN solution. The formamide was determined as formate after base hydrolysis by the quinaldinium iodide method.[15] Dose: 4.92 krad/min.

Discussion

N_2O Solutions. In dilute solutions, the solvated electron yield is 2.7, but saturated N_2O (0.02 M) is sufficiently reactive to scavenge additional electrons from the spurs, giving a yield of about 3.3 from reaction 1, while the total OH yield including 2.8 from the water comes to about 6.1. Other products are H_2 and H_2O_2, found unchanged in the reaction products, and a yield of H atoms amounting to 0.5, which are reported[19] to react very rapidly with cyanide ions. Detailed studies[4,5] have shown that OH radicals add to cyanide ions to form $HOCN^-$, which rapidly protonates and rearranges to the formamide radical $\cdot CONH_2$. The product of $H + CN^-$ is presumably the same as that formed by H + HCN, namely, H_2CN or its basic form HCN^-.

The present results show clearly that the chief reaction product $\cdot CONH_2$ reacts with itself by disproportionation to yield formamide and cyanate

$$2CONH_2 = HCONH_2 + HCNO \qquad (2)$$

The fate of the minor radical H_2CN is not altogether clear because of the uncertainties in the yield data (Table II), but it seems likely that it disappears mainly by reaction with the major radical eventually either to regenerate cyanide or to form two molecules of formamide

$$H_2CN + CONH_2 = 2HCN + H_2O \qquad (3a)$$

$$H_2CN + CONH_2 = HCN + HCONH_2 \qquad (3b)$$

$$H_2CN + CONH_2 + H_2O = 2HCONH_2 \qquad (3c)$$

Nitrogen Solutions. Since the solvated electron formed in water irradiation with a yield $G = 2.7$ does not react with cyanide ion, it must disappear mainly by reaction with other reaction products as they accumulate. Table IV gives reaction rate constants for the electron reactions with various molecules of interest. At pH 11, the 5×10^{-3} M KCN solutions contain in equilibrium 2% HCN, or 10^{-4} M. Table IV shows that this HCN can effectively compete for the electron with cyanate, formamide, and glycine but not with hydrogen peroxide, which could build up only to an insignificant concentration of the order of 10^{-6} M. In fact, peroxide was not found in irradiated solutions unless N_2O was present. The product of the reaction

Table IV. Reported Reaction Rate Constants for Hydrated Electron Reactions

Reaction	K, M^{-1} s^{-1}	Ref
$e^- + CNO^-$	1.3×10^6	20
$e^- + HCN$	2×10^8	6
e^- + glycine (negative ion)	1.7×10^6	21
$e^- + HCONH_2$	4.2×10^7	22
$e^- + H_2O_2 = OH^- + OH$	1.6×10^{10}	23

$e^-_{aq} + HCN$ is the same as from $H + CN^-$, namely, the radical H_2CN.[24]

In these solutions, the radiation will generate, per 100 eV of energy absorbed, 0.45 molecule of H_2, 0.7 H_2O_2, 2.7 e^-_{aq} (hydrated electrons), 2.8 OH radicals, and 0.6 H atoms.[18] The peroxide will consume 0.7 e^-_{aq}

$$e^- + H_2O_2 = OH + OH^- \qquad (4)$$

and thereby generate an additional 0.7 OH. All 3.5 OH react with CN^- to give $CONH_2$. The remaining 2.0 e^-_{aq} react with HCN to give H_2CN, and the 0.6 H react with CN^- to give H_2CN. Thus, initially 6.1 cyanides are converted to 3.5 $CONH_2$ radicals plus 2.6 H_2CN radicals. These radicals can react with themselves, or cross-react with each other (reactions 3), to an extent which depends on the relative magnitudes of the respective rate constants.

The yield of 0.65 cyanate suggests that 1.3 $CONH_2$ disappear by reaction 2 to yield 0.65 cyanate and 0.65 formamide.

The yield of glycine, the most highly reduced of the prominent products, probably arises from the combination of two H_2CN

$$2H_2CN \rightarrow (H_4C_2N_2) \xrightarrow{2H_2O} H_2NCH_2COOH + NH_3$$

Hydrolysis of an intermediate presumably results in the induction period for the appearance of glycine.

We have thus accounted for 1.3 $CONH_2$ and 0.4 H_2CN. The remaining 2.2 $CONH_2$ and 2.2 H_2CN react with each other. To account for the observed yield of cyanide destruction, we postulate that 1.6 $CONH_2$ + 1.6 H_2CN undergo reaction 3a to regenerate 3.2 molecules of cyanide. The remaining 0.6 $CONH_2$ + 0.6 H_2CN form complexes which after some delay react (a) by hydrolysis to yield 0.3 formamide, (b) by polymerization to yield 0.5 HCN as insoluble polymer and 0.4 HCN in the two "unknown" products, assumed to have formulas $H_nC_nN_n$.

Thus the yields of the major products can be reasonably accounted for. Side reactions can be postulated for the small yields of urea, formaldehyde, and cyanamide.

Remarks. The radiation chemistry of cyanide is certainly more complicated than that of the halides. The reaction products, though complex, seem less likely to result eventually in compounds of biological interest than do the reaction products of the spontaneous polymerization of more concentrated aqueous cyanide solutions.[3]

Acknowledgments. Mr. David A. Comstock rendered invaluable assistance throughout this work. Much of the analytical work was accomplished by our summer students Mary Clare Fedarko and Francis D. Gutowski. Thanks are due to Mr. Donald F. Sacker of the Medical Department for his help in the development of x-ray plates.

References and Notes

(1) Research carried out at Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration and supported by its Division of Physical Research.
(2) C. Ponnamperuma in "The Origins of Prebiological Systems", Academic Press, New York, N.Y. 1965, p 221.
(3) (a) J. Oró and A. P. Kimball, *Arch. Biochem. Biophys.*, **94**, 217 (1961); (b) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, **38**, 121 (1968).
(4) D. Behar, *J. Phys. Chem.*, **78**, 2660 (1974).
(5) H. Büchler, R. E. Bühler, and R. Cooper, *J. Phys. Chem.*, **80**, 1549 (1976).
(6) H. Ogura, *Bull. Chem. Soc. Jpn.*, **41**, 2871 (1968).
(7) H. Ogura, T. Fujimura, S. Murozono, K. Hirano, and M. Kondo, *J. Nucl. Sci. Technol.*, **9**, 339 (1972).
(8) B. H. J. Bielski and H. A. Schwarz, *J. Phys. Chem.*, **72**, 3836 (1968).
(9) E. J. Conway, "Microdiffusion Analysis and Volumetric Error", Crosby Lockwood and Son Ltd., London, England, 1962.
(10) A. Appleby and H. A. Schwarz, *J. Phys. Chem.*, **73**, 1937 (1969).
(11) F. G. Carpenter, *Anal. Chem.*, **34**, 66 (1962).
(12) M. W. Scoggins, *Anal. Chem.*, **44**, 1294 (1972).
(13) J. Epstein, *Anal. Chem.*, **19**, 272 (1947).
(14) Orion Research Inc., "Instruction Manual for the Ammonia Electrode", Model 95-10, Cambridge, Mass., 1972.
(15) E. Sawicki, T. W. Stanley, J. Pfaff, and J. Ferguson, Proceedings of the Feigl Anniversary Symposium, Birmingham, England, 1962, p 62.
(16) T. Nash, *Biochem. J.*, **55**, 416 (1953).
(17) I. M. Hais and K. Macek, Ed., "Paper Chromatography", Academic Press, New York, N.Y., 1963.
(18) K. Sehested, E. Bjergbakke, and H. Fricke, *Radiat. Res.*, **56**, 385 (1973).
(19) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).
(20) M. Anbar and P. Neta, *Int. J. Applied Radiat. Isotopes*, **16**, 227 (1965).
(21) E. Hayon and M. Simic, *Intra-Sci.-Chem. Rep.*, **5**, 357 (1971).
(22) E. J. Hart, E. M. Fielden, and M. Anbar, *J. Phys. Chem.*, **71**, 3993 (1967).
(23) R. R. Hentz, Farhataziz, and E. M. Hansen, *J. Chem. Phys.*, **56**, 4485 (1972).
(24) D. Behar and R. W. Fessenden, *J. Phys. Chem.*, **76**, 3945 (1972).