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The Radiation Chemistry of Aqueous Solutions of Simple RCN Compounds

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Abstract: The γ radiolysis of the following RCN compounds in aqueous solutions was studied at low doses (<10 krads): hydrogen cyanide, acetonitrile, propionitrile, malononitrile, and succinonitrile. The radiolytic products H_2, H_2O_2, NH_3, aldehydes, CO_2, and HNO_2 were determined in degassed or oxygenated solutions at pH's 2 and 6. The cyano group was found to be the main target of attack by the primary free-radical products of irradiated water. Its behavior was considered by taking into account the free-radical model of water radiolysis and the radiation chemical yields measured under various experimental conditions. The following rate constants were determined in competition experiments: $k(\mathrm{H} + \mathrm{HCN}) = 3.6 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{e_{eq}}^- + \mathrm{HCN}) = 6.6 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{OH} + \mathrm{HCN}) \leq 5 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$; $k(\mathrm{H} + \mathrm{CH_3CN}) = 3.5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{e_{eq}}^- + \mathrm{CH_3CN}) = 2.5 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{OH} + \mathrm{CH_3CN}) = 5.5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$; $k(\mathrm{H} + \mathrm{C_2H_5CN}) = 1.0 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{e_{eq}}^- + \mathrm{C_2H_5CN}) = 1.0 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{OH} + \mathrm{C_2H_5CN}) = 7.3 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$; $k(\mathrm{H} + \mathrm{CH_2(CN)_2}) = 1.6 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{e_{eq}}^- + \mathrm{CH_2(CN)_2}) = 7.1 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$; $k(\mathrm{H} + \mathrm{(CH_2CN)_2}) = 1.3 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{e_{eq}}^- + \mathrm{(CH_2CN)_2}) = 1.7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, $k(\mathrm{OH} + \mathrm{(CH_2CN)_2}) = 3.0 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. The correlation between Taft's σ^* function and measured rate constants of $\mathrm{e_{eq}}^- + \mathrm{RCN}$ reactions shows that the effect of the substituent R is mainly of the inductive type.

The radiation chemistry of aqueous solutions of RCN molecules is little known, although the versatility of the cyano group was demonstrated in experiments where the energy was supplied by radiation.[1-7] The CN group might have made its appearance in the early stages of the chemical evolution,[1,2] and this explains the interest in chemical changes in aqueous solutions of RCN compounds in prebiotic and radiation studies. In this work we have investigated the behavior of some simple RCN molecules in dilute aqueous solutions exposed to low doses (<10 krads) of ionizing radiations (the cobalt-60 γ-rays). When the dilute aqueous solutions are irradiated the energy is practically deposited in water only. This leads to the formation of the hydrogen atom, hydrated electron, and hydroxyl radical in known radiation chemical yields. Their natures and the sequence of events that take place in irradiated water are well established.[8] This was not only helpful in formulating the reaction mechanism but also in its testing by correlating the energy input, and the yields of primary free radicals, to the measured yields of stable radiolytic products.

The compounds investigated are: HCN, CH_3CN, C_2H_5CN, $CH_2(CN)_2$, and $(CH_2CN)_2$. It was hoped that the variation of the substituent R in the RCN molecule might contribute to a better understanding of the role of the cyano group in processes occurring in irradiated aqueous solutions. Also the previous work with aqueous solutions of $(CN)_2$,[3] where a high reactivity of the hydrated electron was found, suggested that the influence of the adjoining group on the reactivity of $\mathrm{e_{eq}}^-$ toward CN is worth examining.

In order to avoid a larger accumulation of stable radiolytic products, their involvement in the reaction mechanism, and the resulting complication of the reaction scheme, we have carried out the irradiations only at low absorbed doses. An earlier study on the radiolysis of aqueous solutions of hydrogen cyanide[4,5] concerns the γ radiolysis at doses higher than in this work by a factor up to 100. Other published data, relevant

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(7) (a) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 74, 3362 (1970); (b) R. Livingston and H. Zeldes, *J. Magn. Resonance*, 1, 169 (1969).

(8) I. G. Draganić and Z. D. Draganić, "The Radiation Chemistry of Water," Academic Press, New York, N. Y., 1971.

Table I. The Yields of Molecular Products in Deaerated Aqueous Solutions of RCN Determined at Low Radiation Doses

pH	RCN, *M*	$G(H_2)_{meas}$	$G(NH_3)$	G(RCHO)	$G(H_2O_2)$	$G(CO_2)$
HCN						
2	0.10		2.61	1.88		~0.8
	0.08	0.40	2.36	1.78		
	0.04	0.42	2.08	1.29		
Natural	0.10	0.38	2.46	*a*		~0.8
	0.04		1.69			
	0.006[b]	0.42	1.9	1.1[c]		0.8
CH_3CN						
2	0.10	0.51	1.10	0.94	0.83	
	0.05		0.88	0.88		
~6	0.10	0.45	1.00	1.50		<0.1
	0.10[d]		0.40	0.82	0.71	
C_2H_5CN						
2	0.10	0.77	1.10	1.32	0.77	
	0.05		0.80	0.82		
~6	0.10	0.51	1.31	1.50		0.16
	0.05		1.35	1.50		
$CH_2(CN)_2$[e]						
2	0.05					0.67
	0.01	0.51				
~6	0.05	0.31				
	0.01	0.39				0.50
$(CH_2CN)_2$						
2	0.05		0.95			
	0.01	0.60	0.92			
~6	0.05	0.42	1.01			0.1
	0.01	0.44	0.87			

[a] Fast formation of cyanhydrin prevents formaldehyde determination. [b] Reference 5, measured at doses up to 500 krads; $G(-HCN) = 5.8$. [c] Cyanhydrin measured. [d] Solutions N_2O saturated. [e] B. R. Simonović, data obtained as a part of a B.S. thesis at the University of Beograd, 1972.

to the radiation chemistry of aqueous solutions of RCN compounds, refer only to the esr spectra recorded during *in situ* radiolysis of aqueous solutions of HCN,[6] CH_3CN, and C_2H_5CN.[7a]

A study of short-lived intermediates by fast kinetic spectrophotometry and a pulsed electron beam is in progress and will be reported elsewhere.[9]

Experimental Section

The purification of water and glassware was carried out by the standard procedures used in the radiation chemistry of water. The chemicals (Merck, BDH, or Fluka products) were of the highest purity available. Acetonitrile, propionitrile, malononitrile, and succinonitrile were purified by distillation under vacuum. Hydrogen cyanide was freshly prepared prior to use from a known amount of sodium cyanide and deaerated sulfuric acid. A simple setup and the syringe technique were used for the sample preparation and irradiation. The concentration of HCN was determined by argentometric titration.

The syringe technique was used for the preparation of deaerated solutions of propionitrile in order to avoid its loss during degassing.

Irradiations were carried out in a radioactive cobalt irradiation unit, at a dose rate of 1.6×10^{17} eV g^{-1} min^{-1}. Absorbed doses varied between 1.6×10^{17} and 5×10^{17} eV g^{-1}; only for ammonia determinations they amounted up to 20×10^{17} eV g^{-1}.

The gaseous products H_2 and CO_2 were measured by gas chromatography; this technique was also used for the detections of carbon monoxide, nitrogen, nitrous oxide, methane, and ethane. Prior to the determination the gases were extracted from irradiated solution in an evacuated chamber. Small amounts of NaOH or $AgNO_3$ were present when HCN had to be prevented from escaping at lower pressures.

The separation of ammonia from irradiated solution was performed by the Conway diffusion method.[10] Fairly dilute solutions of NaOH were used in order to avoid the hydrolysis of nitriles. In the case of succinonitrile the NaOH concentration was 1×10^{-2} *M;* malononitrile hydrolyzes even under such conditions, and the ammonia determination could not be performed.

The concentration of NH_3 was measured spectrophotometrically by using the Nessler reagent.[11] The molar extinction coefficient slightly varied according to the stock solution; at 400 nm and 24° it was usually 3190 M^{-1} cm^{-1}. Special attention had to be paid to the blanks.

Formaldehyde was measured spectrophotometrically with 2,7-dihydroxynaphthalene as the reagent.[12] The molar extinction coefficient in the presence of 0.1 *M* HCN was 13,500 M^{-1} cm^{-1} at 540 nm and 24°. Acetaldehyde and propionaldehyde were determined spectrophotometrically by using 2,4-dinitrophenylhydrazine as the reagent.[13] The molar extinction coefficients at 24°, in the presence of 0.1 *M* nitrile, were found to be 16,000 M^{-1} cm^{-1} at 436 nm and 13,000 M^{-1} cm^{-1} at 430 nm for acetaldehyde and propionaldehyde, respectively.

Two spectrophotometric methods were used for H_2O_2 determinations. In irradiated solutions of acetonitrile and propionitrile, the measurements could be made with the more sensitive KI method;[14] the molar extinction coefficient in the presence of 0.1 *M* nitrile was 23,470 M^{-1} cm^{-1}, at 350 nm and 24°. The ceric sulfate method, based on the reduction of the cerium(IV) ion (1×10^{-5} *M*) in acid medium (0.8 *N* H_2SO_4),[15] had to be used in solutions of HCN, $CH_2(CN)_2$, and $(CH_2CN)_2$. The change in cerium(IV) concentration was measured at 320 nm; the molar extinction coefficients were 5323 M^{-1} cm^{-1} for HCN and 5600 M^{-1} cm^{-1} for other nitriles. Because of its low sensitivity, this method could be used for measurements in oxygenated solutions only. For comparison, both KI and ceric methods were used for determinations in oxy-

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(10) E. J. Conway, "Microdiffusion Analysis and Volumetric Error," Van Nostrand, New York, N. Y., 1947.

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Table II. The Yields of Molecular Products in Oxygenated (1×10^{-3} *M*) Aqueous Solutions of RCN Determined at Low Radiation Doses

pH	RCN, *M*	$G(H_2)_{meas}$	$G(NH_3)$	G(RCHO)	$G(H_2O_2)$	$G(HNO_2)$ *a*	$G(HNO_2)$ *b*	$G(CO_2)$
				HCN				
2	0.10		0.92	0.0	2.0	1.75	<2.1	1.0
	0.04		0.70	0.0	1.5		<1.9	
Natural	0.10	0.39	0.68	*c*	1.9	1.0	<1.2	1.2, 1.2[d]
	0.04		0.45		1.5		<1.3	
				CH_3CN				
2	0.25				2.75	0.1	<0.2	
	0.10	0.41	0.35	0.76	2.75			
~6	0.25				2.15	0.1	<0.15	<0.1[d]
	0.10	0.41	0.36	0.86	2.33			0.12
				C_2H_5CN				
2	0.10		0.30	0.80	2.75	0.1	<0.4	
	0.05				2.83		<0.1	
~6	0.10	0.45	0.30	3.0	1.70	0.1	<0.4	1.0
	0.05			2.7	1.70		<0.3	0.29[d]
				$CH_2(CN)_2$[e]				
2	0.05				1.2		<0.6	
	0.01				1.2		<0.6	
~6	0.05				1.2		<0.7	5.5, 2.2[f]
	0.01				1.2	0.4	<0.5	3.9
				$(CH_2CN)_2$				
2	0.05		0.1		1.80		<0.2	
	0.01				1.74		<0.1	
~6	0.05		0.1		1.80	0.1	<0.2	0.83, 0.28[d]
	0.01				1.70		<0.1	

[a] Direct measurement. [b] Derived from ceric reduction. [c] Fast formation of cyanhydrin prevents formaldehyde determination. [d] Solution contains 1×10^{-4} *M* O_2 and 2.5×10^{-2} *M* $NaNO_3$. [e] Table I, footnote *e*. [f] Solution contains 0.1 *M* $(CH_3)_2CHOH$.

genated solutions of acetonitrile; the measured H_2O_2 values were in agreement within the limits of experimental error.

Nitrite ion concentration was determined spectrophotometrically by the method described by Rider and Mellon.[16] For comparison, although less accurate, the concentration of the nitrite ion was also derived from the reduction of cerium(IV) in acid medium. This reaction was carried out similarly to the above-mentioned H_2O_2 determination, only the optical density readings were made 30 min after adding the reagent, since here the reduction proceeds more slowly.

In searching for oximes, hydroxamic acid, and hydroxylamine, we have developed a procedure based on the reactions specific for the =C=NOH group.[17] When aldoximes or hydroxamic acids are heated with concentrated hydrochloric acid, the oxime group splits up to give hydroxylamine hydrochloride. In the presence of acetic acid-sodium acetate buffer, this product is oxidized by iodine to nitrous acid and the HNO_2 is determined as described above. As shown by an analysis of artifical mixtures containing 10^{-5} *M* =C=NOH compounds, the procedure of splitting is not quantitative and the loss can amount up to about 30%.

The radiation chemical yield of a product P is the number of species produced per 100 eV of energy absorbed; it is denoted by *G*(P). Each yield quoted in this work was derived from a series of at least five separate experiments. If not otherwise specified, the radiation chemical yields were calculated from the slopes of concentration-dose plots which were linear over the dose range studied. It should be mentioned that $G(H_2)_{meas}$ denotes the yield of H_2 measured in solutions, while $G(H_2)$ refers to pure water, *i.e.*, to the primary molecular hydrogen yield.

Results

Table I shows the radiation chemical yields of stable molecular products measured at low radiation doses in deaerated aqueous solutions. The corresponding data for solutions containing oxygen are summarized in Table II.

It should be pointed out that the variations of CO_2 concentration in blanks of deaerated solutions of HCN were fairly large. The reason for this is not clear and the reported $G(CO_2)$ are an estimation only. The blanks did not vary with time; furthermore, the variations mentioned above were smaller in oxygenated solutions.

Carbon dioxide and molecular hydrogen were also measured in competition experiments on solutions containing various concentration ratios of RCN and ethanol, hydronium ion, or formate ion. These data were used for the rate constant determinations of reactions studied.

The irradiated solutions were checked for some other compounds that might be formed under our working conditions. Spectrophotometric methods gave a negative answer as to the formation of oximes, hydroxamic acid, and hydroxylamine. The optical absorbancies of the solutions studied were recorded before and after irradiation; some weak, unidentified absorbancies were registered at short uv wavelengths (<220 nm). They were dose dependent, and in HCN solutions they changed with time after irradiation. Carbon monoxide was sought in deaerated solutions of HCN (0.08 *M*) and, if present, its yield should be lower than 0.1 G unit. Also, negative answers were obtained by the gas chromatographic method of detecting N_2, N_2O, CH_4, and C_2H_6 in 0.1 *M* solutions of acetonitrile or propionitrile, in the presence or absence of oxygen.

Discussion

Reaction of RCN with the Primary Free-Radical Products of Water Radiolysis. The absence of CH_4 and C_2H_6, and the low values (Table I) of molecular

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(16) B. Rider and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 96 (1946).

(17) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, Amsterdam, 1966, p 286.

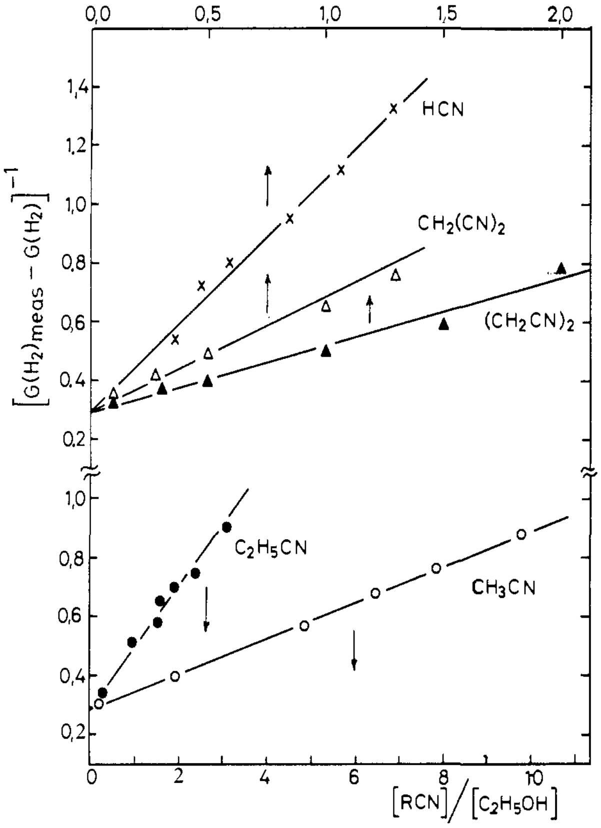

Figure 1. Competition between RCN and C_2H_5OH for H atoms. Molecular hydrogen yields measured at pH 2 and various solute concentration ratios.

hydrogen yield, $G(H_2)_{meas} \sim G(H_2)$, show that the cyano group in the RCN molecules studied is the main target of attack of primary reducing radicals.

$$RCN + H \longrightarrow RC(H){=}\dot{N} \text{ (or } R\dot{C}{=}NH) \quad (1)$$

$$RCN + e_{aq}^- \longrightarrow (RCN)^- \quad (2)$$

$$(RCN)^- + H_2O \longrightarrow RC(H){=}\dot{N} \text{ (or } R\dot{C}{=}NH) + OH^- \quad (2a)$$

The free radical $RC(H){=}\dot{N}$ was identified by esr technique in solutions of HCN,[6] CH_3CN, and C_2H_5CN,[7a] in experiments pertaining to radicals with an average lifetime of 500 μsec. The species $R\dot{C}{=}NH$ and $(RCN)^-$ were suggested in faster pulse radiolytic experiments with $(CN)_2$.[3]

The values of $G(H_2)_{meas}$ somewhat lower than 0.45, the primary H_2 yield, are in agreement with other observations[18] on the formation of $G(H_2)$ at increased reactivities toward e_{aq}^-.

Table I also shows that some $G(H_2)_{meas}$ values at pH 2 are higher than the primary H_2 yield, 0.51–0.77, pointing to a less important additional source of molecular hydrogen. This could be the reaction of hydrogen abstraction from the substituent R, a slow reaction in competition with the one represented by eq 1. Such reaction was reported for CH_3CN[19] where it was found to be unimportant. As it will be seen from the analysis of the experimental data shown in Table I, the abstraction reactions are more significant for some other studied RCN molecules. Nevertheless, eq 1 represents in a satisfactory manner the fate of H atoms, since more than 90% disappear by addition to the cyano group.

The rate constants for reaction 1 were determined by observing its competition with the reaction

$$C_2H_5OH + H \longrightarrow H_2 + C_2H_4OH \quad (3)$$

The molecular hydrogen yields were measured in solutions containing various concentration ratios of RCN and ethanol at pH 2. Experimental data were plotted in Figure 1 according to the competition relation

$$[G(H_2)_{meas} - G(H_2)]^{-1} = \frac{1}{G(H)}\left\{1 + \frac{k_1[RCN]}{k_3[C_2H_5OH]}\right\} \quad (4)$$

The rate constants for various RCN compounds, calculated from these competition plots, are summarized in Table III.

Table III. Rate Constants of Reactions between RCN and Primary Free-Radical Products of Water Radiolysis[a]

RCN	$k(H + RCN)$, M^{-1} sec^{-1}	$k(e_{aq}^- + RCN)$, M^{-1} sec^{-1}	$k(OH + RCN)$, M^{-1} sec^{-1}
HCN	3.6×10^7	6.6×10^8	$\leq 5 \times 10^7$
	3×10^7 [b]	2×10^8 [b]	
CH_3CN	3.5×10^6	2.5×10^7	5.5×10^6
	2.7×10^6 [c]	3×10^7 [d]	
	1.5×10^6 [e]		
C_2H_5CN	1.0×10^7	1.0×10^8	7.3×10^7
	1.06×10^7 [e]	1.5×10^8 [d]	
$CH_2(CN)_2$	1.6×10^7 [f]	7.1×10^9 [f]	
$(CH_2CN)_2$	1.3×10^7	1.7×10^9	3.0×10^7

[a] Absolute values of rate constants measured in this work were calculated by taking $k(H + C_2H_5OH) = 1.65 \times 10^7\ M^{-1}\ sec^{-1}$, $k(e_{aq}^- + H_3O^+) = 2.25 \times 10^{10}\ M^{-1}\ sec^{-1}$, and $k(OH + HCOO^-) = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$. [b] Reference 5. [c] Reference 19. [d] Reference 25. [e] Reference 24. [f] Table I, footnote *e*.

The rate constants of reaction 2 were determined by measuring its competition with the reaction

$$H_3O^+ + e_{aq}^- \longrightarrow H + H_2O \quad (5)$$

in solutions containing ethanol; the solutions pH's were 3–4 and the ionic strength constant (μ) was 0.002. Experimental H_2 yields and the expression

$$[G(H_2)_{meas} - G(H_2) - G(H)]^{-1} = \frac{1}{G(e_{aq}^-)}\left\{1 + \frac{k_2[HCN]}{k_5[H_3O^+]}\right\} \quad (6)$$

were used in constructing the competition plots like those shown in Figure 1. The rate constants derived from these measurements are given together with other values in Table III.

As regards the reaction of RCN with the hydroxyl radical, the present results are not sufficient to distinguish between two possible mechanisms. The first is the addition reaction such as in the case of hydrogen cyanide, $HCN + OH \rightarrow HC(OH){=}\dot{N}$ (or $H\dot{C}{=}NOH$); the radical $HC(OH){=}\dot{N}$ was identified by esr technique.[6] The second mechanism refers to the hydrogen atom abstraction from the α position, such as apparently occurs in the case of propionitrile, $CH_3CH_2CN + OH \rightarrow CH_3\dot{C}HCN + H_2O$, although not in the case of the acetonitrile.[7a] The radicals formed by abstraction of α hydrogens were found by paramagnetic resonance measurements of concentrated aqueous solutions of

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(18) Z. D. Draganić and I. G. Draganić, *J. Phys. Chem.*, **75**, 3950 (1971).

(19) P. Neta, G. R. Holdren, and R. H. Schuler, *J. Phys. Chem.*, **75**, 449 (1971).

various nitriles photolyzed with ultraviolet light.[7b] However, we think that in the radiolysis of dilute solutions the hydrogen atom abstraction from R is, like in the case of H atom reactions, less important than the addition of OH to the cyano group.

$$\mathrm{RCN} + \mathrm{OH} \longrightarrow \mathrm{RC(OH){=}\dot{N}}\ (\text{or } \mathrm{R\dot{C}{=}NOH}) \qquad (7)$$

This reaction can account for the formation of ammonia and carbon dioxide in solutions containing the scavengers for e_{aq}^-, oxygen, and nitrate ion (Table II) or nitrous oxide (Table I).

The rate constants for reaction 7 were determined from competition plots similar to those given in Figure 1. The reaction used was[20]

$$\mathrm{HCOO^-} + \mathrm{OH} \longrightarrow \mathrm{OH^-} + \mathrm{H\dot{C}OO} \xrightarrow{\mathrm{NO_3^-}} \mathrm{CO_2} + \mathrm{HNO_3^-} \qquad (8)$$

The irradiated solutions consisted of RCN and formate at various concentration ratios and contained $NaNO_3$ (2.5×10^{-2} *M*) and O_2 (about 10^{-4} *M*). The measured product was carbon dioxide and the competition plots were made according to the relation

$$[G(\mathrm{CO_2})]^{-1} = \frac{1}{G(\mathrm{OH})}\left\{1 + \frac{k_7[\mathrm{RCN}]}{k_8[\mathrm{HCOO^-}]}\right\} \qquad (9)$$

In the calculation of $G(\mathrm{CO_2})$ the contribution of the $\mathrm{H} + \mathrm{HCOO^-}$ reaction has been taken into account; the corrections were calculated from an expression which has been used previously in a similar case.[20] Higher CO_2 yields in oxygenated solutions of hydrogen cyanide and of the malononitrile prevented us from using eq 9 here and obtaining the competition plots; nevertheless, for $k(\mathrm{OH} + \mathrm{HCN})$ an estimation could be made.

The Influence of Substituent R on the Rate of Reaction $e_{aq}^- + \mathrm{RCN}$. The cyano group is strongly polarized in such a way that the carbon atom is a positive, thus electrophilic, site, and the nitrogen is negative. If the hydrated electron indeed reacts by addition to the cyano group, it is to be expected that the substituent R should affect the rate constant of this reaction. Taft's empirical relation[21] provides a criterion: $\log k = \log k_0 + \sigma^*\rho^*$. Here, k and k_0 in $M^{-1}\ \mathrm{sec}^{-1}$ are the rate constants for reactions $e_{aq}^- + \mathrm{RCN}$ and $e_{aq}^- + \mathrm{CH_3CN}$, respectively; σ^* is Taft's function, the polar substituent constant which represents a measure of the inductive electron-withdrawing power of the group R in the molecule, $\sigma_{\mathrm{CH_3}}^* = 0$ by definition; ρ^* is a constant giving the susceptibility of a given reaction series to polar substituents. It is specific for the given reaction center and attacking reagent, which are in this case the cyano group and hydrated electron, respectively.

Figure 2 shows the correlation between the measured rate constants and Taft's σ^* function. The σ^* function was not available for succinonitrile. In estimating the value for the CH_2CH_2CN substituent we have taken the known value for CH_2CN and a finding on several series of CH_2 containing compounds,[21] which states that the interposition of a methylene group leads to the reduction of the inductive effect of a substituent by a factor of approximately 2.8.

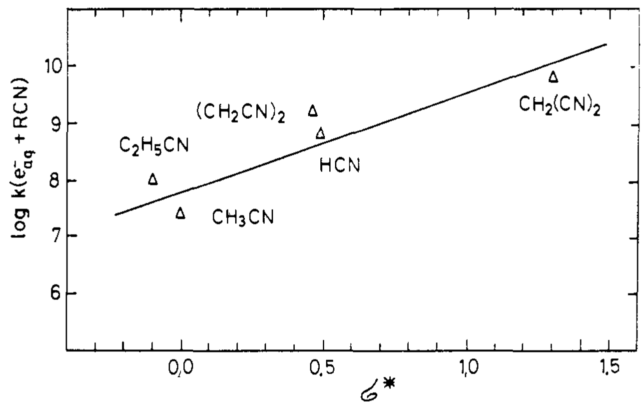

Figure 2. Correlation between Taft's σ^* function and the e_{aq}^- rate constants of studied RCN compounds.

The number of experimental values is rather limited but the data cover a wider range of σ^* values. They suggest that the inductive effect of substituent R is the main factor determining the rates of reactions between the hydrated electron and the simple RCN compounds, both mononitriles and dinitriles. Due to the scarcity of studies of the same nature it is difficult to compare the value of 1.7, calculated for ρ^* from the above data, with those of other workers. It may be noted, however, that the ρ^* value for the reactions of e_{aq}^- with the undissociated carboxylic acids is 1.94,[22] which is the same sign and order as the value reported here. In both cases, *i.e.*, the reactions with the cyano or the carboxylic group, the hydrated electron attacks the positive carbon atom in the reaction center.

Reactions of the Secondary Free Radicals $\mathrm{RC(H){=}\dot{N}}$ (or $\mathrm{R\dot{C}{=}NH}$) and $\mathrm{RC(OH){=}\dot{N}}$ (or $\mathrm{R\dot{C}{=}NOH}$). The yields of stable products at acid and neutral pH's (Table I) suggest that, in considering the reaction mechanism, the free radical produced in reactions of primary reducing species (H or e_{aq}^-) with RCN can be adequately represented as $\mathrm{RC(H){=}\dot{N}}$ (or $\mathrm{R\dot{C}{=}NH}$). This is to be expected if reaction 2a is sufficiently fast or the products of $(\mathrm{RCN})^-$ reactions hydrolyze and form the same products as those originating in reactions of H atom adducts.

The yield dependence on the solute concentration is fairly weak (Table I) and shows that the secondary free radicals should partly disappear in the following reactions with solute

$$\mathrm{RC(H){=}\dot{N}}\ (\text{or } \mathrm{R\dot{C}{=}NH}) + \mathrm{RCN} \longrightarrow \text{products} \qquad (10)$$

and

$$\mathrm{RC(OH){=}\dot{N}}\ (\text{or } \mathrm{R\dot{C}{=}NOH}) + \mathrm{RCN} \longrightarrow \mathrm{RC(H){=}\dot{N}} + \mathrm{ROCN}\ (\text{or } \mathrm{RNCO}) \qquad (11)$$

The disproportionation

$$2\mathrm{RC(H)\dot{N}}\ (\text{or } 2\mathrm{R\dot{C}{=}NH}) \longrightarrow \mathrm{RCN} + \mathrm{RHC{=}NH} \qquad (12)$$

is supported by the observed yields of aldehyde and ammonia, originating in the hydrolysis of imine from reaction 12

$$\mathrm{RHC{=}NH} + \mathrm{H_2O} \longrightarrow \mathrm{RCHO} + \mathrm{NH_3} \qquad (13)$$

and the substituted imine, a possible product of reaction 10

$$\mathrm{RHC{=}NR} + \mathrm{H_2O} \longrightarrow \mathrm{RCHO} + \mathrm{RNH_2} \qquad (14)$$

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[20] Z. Draganić and I. Draganić, *J. Phys. Chem.*, 77, 765 (1973).

[21] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

[22] O. Mićić and V. Marković, *Int. J. Radiat. Phys. Chem.*, 4, 43 (1972).

The disproportionation or dimerization of the OH adduct

$$2RC(OH){=}\dot{N}\ (\text{or } R\dot{C}N{=}OH) \longrightarrow \begin{cases} RCN + RC(OH){=}NOH & (15)\\ P_{16}, \text{ where } P_{16} \text{ is a dimer} & (16)\end{cases}$$

is in competition with reaction 11. The low yields of CO_2, produced by the hydrolysis of ROCN

$$ROCN\ (\text{or } RNCO) + H_2O \longrightarrow CO_2 + RNH_2 \qquad (17)$$

suggest also the condensation reaction[23]

$$n ROCN\ (\text{or } RNCO) \longrightarrow P_{18} \qquad (18)$$

The importance of reactions 16 and 18, where unidentified dimers and condensation products are formed, can be seen from the facts that the CO_2 yields are fairly low and that oximes and hydroxamic acid are absent.

Comments on Radiolytic Mechanisms of the Systems Studied. Equations 1, 2, 7, and 10–18 represent a general case of radiolytic behavior of RCN in irradiated aqueous solutions in the absence of oxygen. The experimental data are sufficient to account for the predominant paths of the reaction mechanism in individual cases.

Hydrogen Cyanide. HCN reacts with H, e_{aq}^-, and OH through the radical addition to the cyano group (eq 1, 2, and 7). The intermediates disappear by reacting with HCN (eq 10 and 11) in a competition with disproportionation (eq 12, 15, and 16), producing compounds that hydrolyze (eq 13, 14, and 17) and lead to ammonia, formaldehyde, and CO_2. We see in Table I that in degassed solutions $G(NH_3) > G(HCHO)$ and that $G(CO_2)$ corresponds roughly to the excess of ammonia over aldehyde yields. These findings, as well as some data on oxygenated solutions, point to the importance of hydroxyl adduct contribution to the formation of formaldehyde and ammonia. The fact that the yields of ammonia and of formaldehyde are lower than those to be expected from the known yields of primary free radicals suggests that the disappearance of H and OH adducts by reactions 10 and 16 is significant. This conclusion may be also drawn from the data obtained at larger doses;[4,5] the number of HCN decomposed per 100 eV was found to be 5.8, while the yields of products do not differ considerably from ours (Table I).

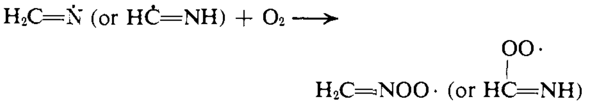
The molecular hydrogen yields (Tables I and II) correspond to the $G(H_2)$ at given reactivities toward primary reducing species[18] and show that there is no additional source of H_2, *i.e.*, that only addition reactions (eq 1 and 2) take place.

The higher yields of hydrogen peroxide in oxygenated solutions are due to the well-established sequence of reactions

$$O_2 + H\ (\text{or } e_{aq}^-) \longrightarrow HO_2\ (\text{or } O_2^-) \qquad (19)$$

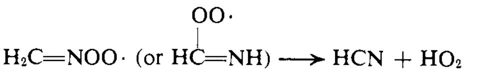
$$2HO_2\ (\text{or } O_2^-) \longrightarrow H_2O_2 + O_2 \qquad (20)$$

Oxygen also reacts with the H atom adduct



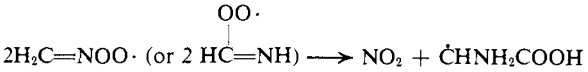
$$H_2C{=}\dot{N}\ (\text{or } H\dot{C}{=}NH) + O_2 \longrightarrow H_2C{=}NOO\cdot\ (\text{or } \overset{OO\cdot}{HC}{=}NH) \qquad (21)$$

while the peroxy radicals decompose



$$H_2C{=}NOO\cdot\ (\text{or } \overset{OO\cdot}{HC}{=}NH) \longrightarrow HCN + HO_2 \qquad (22)$$

and/or react in a sequence of reactions leading to nitrite, nitrate, and some unidentified larger molecules, possibly amino acids P_{25}.

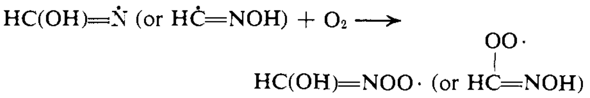


$$2H_2C{=}NOO\cdot\ (\text{or } 2\ \overset{OO\cdot}{HC}{=}NH) \longrightarrow NO_2 + \dot{C}HNH_2COOH \qquad (23)$$

$$2NO_2 \xrightarrow{H_2O} NO_2^- + NO_3^- + 2H^+ \qquad (24)$$

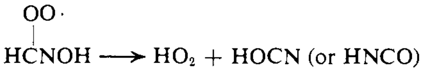
$$\dot{C}HNH_2COOH \xrightarrow{HCN,\ H_2O} P_{25}, \text{ where } P_{25} \text{ are amino acids} \qquad (25)$$

The yields in Table II also show that oxygen reacts with hydroxyl radical adduct



$$HC(OH){=}\dot{N}\ (\text{or } H\dot{C}{=}NOH) + O_2 \longrightarrow HC(OH){=}NOO\cdot\ (\text{or } \overset{OO\cdot}{HC}{=}NOH) \qquad (26)$$

After intramolecular rearrangements the peroxy radicals decompose



$$\overset{OO\cdot}{HC}NOH \longrightarrow HO_2 + HOCN\ (\text{or } HNCO) \qquad (27a)$$

$$HC(OH){=}NOO\cdot \longrightarrow H\dot{C}OO + HNO \qquad (27b)$$

These reactions are followed by reactions 17, 18, 20, and

$$H\dot{C}OO + O_2 \longrightarrow HO_2 + CO_2 \qquad (28)$$

The unstable free acid HNO leads, in the presence of oxygen, to HNO_2 and HNO_3 formation.

It should be mentioned that the only published values for $k(H + HCN)$ and $k(e_{aq}^- + HCN)$, respectively 3×10^7 and $2 \times 10^8\ M^{-1}\ sec^{-1}$, were also obtained by competition in the γ radiolysis.[5] Nevertheless, the agreement with the data in Table III is poor, especially if a more recent value for $k(H + 2\text{-propanol})$ is taken into account[24] and the reported value for $k(H + HCN)$ adjusted. A possible reason might lie in the dose ranges over which the competitions were studied; also, at larger doses stable products can be involved in the competition, particularly in dilute solutions and at higher decomposition of the competing solute.

Acetonitrile and Propionitrile. From $G(H_2)_{meas}$ in Table I it can be estimated that about 2% of the H atoms react according to the reaction

$$CH_3CN + H \longrightarrow H_2 + \dot{C}H_2CN \qquad (29)$$

with $k_{29} \sim 6 \times 10^4\ M^{-1}\ sec^{-1}$. This is in a fair agreement with $3 \pm 1\%$ and $8 \times 10^4\ M^{-1}\ sec^{-1}$, obtained in more reliable experiments where the rates were measured relative to the rate of HD formation from deuterioisopropyl alcohol as competitor.[19] The present data suggest that about 9% of the H atoms react with propionitrile as follows

$$CH_3CH_2CN + H \longrightarrow H_2 + CH_3\dot{C}HCN \qquad (30)$$

with a $k_{30} \sim 9 \times 10^5\ M^{-1}\ sec^{-1}$.

The information on reactions 29 and 30 shows, nevertheless, that here the cyano group is the main point of attack and that the H atom adducts are the principal

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[23] P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1965, p 234.

[24] P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, 75, 1654 (1971).

secondary radicals. The fact that the yields of ammonia and aldehyde do not differ considerably points to the importance of the sequence of reactions 12 and 13. Reactions 10 and 14 can account for the fact that some aldehyde yields are higher than the yields of NH_3.

The experiments with N_2O saturated solutions of CH_3CN (Table I), where $N_2O + e_{aq}^- \rightarrow OH + OH^- + N_2$ show that CH_3CHO and NH_3 are formed even in the absence of hydrated electrons.

The higher yields of H_2O_2 in oxygenated solutions originate in reactions 19 and 20. Also, the formation of peroxy radicals takes place in reactions similar to eq 21 and 22 and followed by reaction 20 contributes to H_2O_2 formation. Some $RHC{=}NO_2\cdot$ disappears by disproportionation and the sequence of reactions, represented by eq 23–25, should take place. The reaction of oxygen with OH adduct, similar to reaction 26, is followed by intramolecular rearrangement and decomposition of the peroxy radicals. These reactions can qualitatively account for the formation of aldehyde and other products observed in oxygenated solutions. Only small amounts of nitrite were found and this fact, together with the absence of N_2 and N_2O, suggests that some RNO_2 compounds should be formed.

The rate constants of H atom reactions with acetonitrile and propionitrile determined in this work (Table III) agree reasonably with the published data obtained by the esr technique[24] or chemical competition.[19] This is also the case with the corresponding constants of hydrated electron reactions obtained by the pulsed electron beam technique.[25]

Malononitrile and Succinonitrile. It seems that also in the case of dinitriles the radiation induced chemical changes follow the same pattern: the attack of primary free radicals on the cyano group, and the formation of the H and OH adducts and their disappearance by disproportionation and in reactions with the solute. The reactions of hydrogen abstraction are not significant. From the H_2 yields in Table I it can be calculated that about 3% of the H atoms react according to

$$CH_2(CN)_2 + H \longrightarrow \dot{C}H(CN)_2 + H_2 \qquad (31)$$

and about 5% in the case of succinonitrile

$$(CH_2CN)_2 + H \longrightarrow CN\dot{C}HCH_2CN + H_2 \qquad (32)$$

In this calculation we had to take into account the correction for depressed formation of primary H_2 yields[18] at higher reactivities of malononitrile and succinonitrile. One can also calculate that $k_{31} \sim 5 \times 10^5$ M^{-1} sec^{-1} and $k_{32} \sim 6 \times 10^5$ M^{-1} sec^{-1}.

It is interesting to note (Table II) the strong decrease of $G(CO_2)$ in solutions containing an efficient OH scavenger. It confirms the importance of the OH adduct also in irradiated dinitrile solutions.

Concluding Remarks

1. Even low doses of ionizing radiations are sufficient to initiate a large variety of chemical changes in aqueous solutions of simple RCN compounds. Regardless of the chemical nature of the substituent R, the cyano group is the main target of attack by the primary free radicals from irradiated water. The analysis of stable product yields supports these conclusions; the Taft's relation also provides an evidence for hydrated electron reactions.

2. Main reactive species are the H, e_{aq}^-, and OH adducts, *i.e.*, the secondary free radicals $RC(H){=}\dot{N}$ (or $R\dot{C}{=}NH$), $(RCN)^-$, and $RC(OH){=}\dot{N}$ (or $R\dot{C}{=}NOH$). By disproportionations, dimerizations, and reactions with solutes, they are responsible for the complexity of the phenomena observed. If the terrestrial crust radioactivity was indeed one of the important energy sources for primary chemical evolution, then these species might have played an important role in prebiotic chemistry.

3. The free-radical model of water radiolysis offers a useful tool for studying the behavior of the cyano group in irradiated water. Since other types of energy deposited in water, *e.g.*, by uv radiation, might induce similar reactions, the approach through the radiolysis of RCN solutions might be of some more general importance and deserves further study.

Acknowledgment. The authors wish to thank Professor A. Stojiljković, University of Beograd, for useful discussions and Mr. M. Borovićanin and Mr. N. Stanĉiĉ for technical assistance.

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[25] E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1970, p 238.