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WITH NUCLEAR EXPLOSIONS

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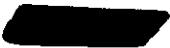
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UNCLASSIFIED**PULSE RADIOLYSIS OF CHLOROFORM
WITH NUCLEAR EXPLOSIONS⁽¹⁾**

Ned E. Bibler

Savannah River Laboratory
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Aiken, South Carolina 29801**ABSTRACT**

Pure degassed chloroform was irradiated by the intense radiation pulse from a nuclear explosion, with the dose estimated to be in the range of 10^5 to 10^6 rads. Good agreement among the organic product yields was obtained for samples exposed in three nuclear tests. In contrast to published results at lower doses/pulse, CCl_4 is the most abundant product. It is proposed that part of the increased CCl_4 yield results from radical recombination reactions involving CCl_3 radicals and Cl atoms. Evidence is presented suggesting that the recombination of CHCl_2 and Cl radicals is also occurring. After including the two radical recombination reactions and a contribution from interaction with neutrons in the pulse, the yields are consistent with the free radical mechanism of the decomposition developed at low dose rates. This consistency is substantiated by the reasonable agreement between the observed yields and those calculated from the mechanism.

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INTRODUCTION

The effect of dose rate on product yields in the radiolysis of chloroform has been studied extensively⁽²⁻⁴⁾. The investigations showed that as the dose rate increases, the 100-eV yields decrease for CH_2Cl_2 and C_2Cl_6 , increase for sym- $\text{C}_2\text{H}_2\text{Cl}_4$ and C_2HCl_5 , and are unchanged for C_2Cl_4 and CCl_4 . The variations are consistent with the fact that high dose rates favor occurrence of radical recombination reactions at the expense of radical solvent reactions⁽⁵⁾. Calculations of the effect of dose rate on the product yields in chloroform have substantiated that in the range of dose rates from 1.3×10^{15} ⁽²⁾ to 1.7×10^{17} eV/g-sec⁽³⁾, the variations result from a competition for CHCl_2 radicals between the solvent and the organic free radicals distributed homogeneously throughout the solution. All the inorganic radicals (Cl atoms) formed by radiolysis of chloroform react with the solvent^(2,6). Even at dose rates of a factor of 10^7 higher, all the Cl atoms still react with the solvent⁽³⁾, although 95% of the organic radicals undergo radical recombination reactions, as compared to 30% at 1.3×10^{13} eV/g-sec⁽²⁾. The instantaneous radical concentrations necessary to initiate a competing process for Cl atoms were not attained at the higher dose rates because of the low dose/pulse available with pulsed X-rays⁽³⁾ (1.9×10^3 rads) and the high reactivity of Cl atoms to chloroform.

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This article describes the radiolysis of chloroform by the intense radiation pulse from a nuclear explosion. The estimated dose/pulse was approximately 200 times larger than in the experiments with pulsed X-rays. The pulse from a nuclear explosion is the largest dose/pulse achieved for electromagnetic radiation and is as large as the dose/pulse deposited by electron accelerators⁽⁷⁾. Evidence was obtained for the competition for Cl atoms between radical recombination and radical solvent reactions. The results are similar to those briefly reported earlier⁽⁶⁾ except that in the present study it is established that CCl₄ is one of the more abundant products.

EXPERIMENTAL

Details of the purification of the chloroform, the preparation of samples, and the analysis of the radiolytic products have been described⁽³⁾. The only impurity in the chloroform was 1, 2-C₂H₄Cl₂ at $\sim 10^{-3}$ mole %. The samples (approximately 1 ml) were sealed in "Pyrex"* tubes (8 mm outside diameter by 5 cm long), which were sealed in wax and enclosed in steel secondary containers (2.5 to 5.0 cm outside diameter by 20.0 cm long) to protect the samples from mechanical shock. Samples were irradiated in conjunction with underground nuclear tests at the U. S. Atomic Energy Commission test site in Nevada. The sample cylinder was positioned so that the prompt radiation from the detonation passed through its length. The distance from the sample cylinder to the device was large enough to assure that there was no effect from the heat generated by the explosion.

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RESULTS

The yields of all the organic products resulting from the irradiation of several samples in three different nuclear tests are presented in Table I. Because the dose received by the samples from the nuclear tests was not determined independently, all the results were normalized to the same amount of chloroform decomposed, i.e., assuming $G(-CHCl_2) = 10.0$. The relative yield was calculated from the expression

$$R(P_i) = 10 [P_i] / \sum_i n_i [P_i]$$

where,

$R(P_i)$ = the relative yield of the i th product

$[P_i]$ = its observed molar concentration

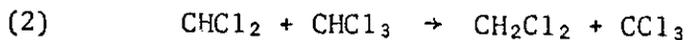
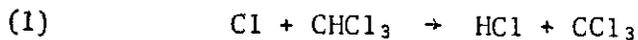
n_i = the number of carbon atoms that it contains

The total amount of decomposition induced in each sample was 0.01 to 0.03 mole %, suggesting doses on the order of 10^5 to 10^6 rads. This value appears reasonable considering published data for possible doses from fusion and fission devices⁽⁹⁾. The time width of the major radiation pulse was probably in the range of 10^{-6} ⁽¹⁰⁾ to 10^{-7} ⁽¹¹⁾ sec. After irradiation, radioactivity was induced in the samples by the neutrons in the pulse. The fraction of radiolytic decomposition due to the induced activity was estimated to be less than 4% of the total decomposition. The only long-lived activity was ^{22}Na (half-life = 2.6 yr), produced by an $(n, 2n)$ reaction with ^{23}Na in the glass.

The dose from the neutrons was estimated by assuming that the neutron flux was on the order of 10^{14} neutrons/cm², a value comparable with published values⁽¹²⁾. From the compilation by Ritts, Solomito, and Stevens⁽¹³⁾ of the coefficients for the dose absorbed by various elements from a monoenergetic neutron beam, coefficients for energy absorption by chloroform were calculated. For neutrons from the fission of ²³⁵U (neutrons of average energy ~ 1.6 MeV⁽¹⁴⁾), the coefficient is 0.30 ergs/g per 10^7 neutrons. For neutrons from the fusion process (2.5 MeV or 14 MeV), values up to four times as large are calculated. From these considerations, it appears that the dose due to neutrons will be greater than 3×10^4 rads and consequently may form a significant fraction (>10%) of the total dose.

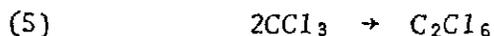
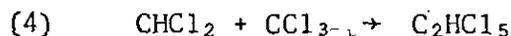
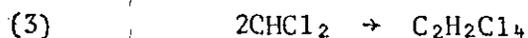
DISCUSSION

The mechanism for the gamma radiolysis of chloroform has been developed from the effects of temperature^(2,6), dose rate^(2,3), and the presence of Cl₂ and Br₂ as radical scavengers⁽⁶⁾ on product yields. The most abundant free radical intermediates formed by ionization, charge neutralization, and neutral excitation processes in chloroform are CHCl₂ and Cl radicals. Each of the free radical intermediates can abstract H atoms from the parent compound to produce the other abundant reactive intermediate, CCl₃ radicals.

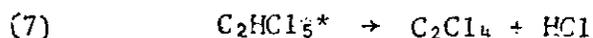
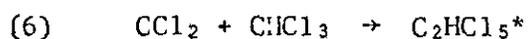


The chloroethane products are then formed by radical recombination reactions.

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For the formation of C_2Cl_4 , Reactions 6 and 7 have been proposed⁽⁶⁾.



For formation of CCl_4 , a charge neutralization reaction involving a scavengeable positive ion has been proposed⁽¹⁵⁾.

The results of the pulsed irradiations in the nuclear tests are consistent with the above mechanism after inclusion of reactions capable of competing with Reaction 1 for Cl atoms. When the results of nuclear tests are compared with those obtained with the pulsed X-rays⁽³⁾ (Table I), a relatively large increase in $R(\text{CCl}_4)$ is observed which suggests the occurrence of a reaction to produce CCl_4 in addition to the charge neutralization reaction. Reaction 8 is proposed.



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Reactions 9 and 10 may also occur.



The net effect of these three reactions is to increase $R(\text{CCl}_4)$ significantly. Not only is CCl_4 one of the products of this set of reactions, but also their occurrence lowers the induced decomposition of the chloroform by lowering the contribution of Reaction 1. Decreasing the induced decomposition of CHCl_3 would cause the relative yields of all the products to increase; however, values for $R(\text{CHCl}_3)$ and $R(\text{C}_2\text{Cl}_6)$ decrease because of the lower efficiency for CCl_3 production by Reaction 1. The values for $R(\text{C}_2\text{Cl}_4)$ increase as expected if they were affected only by the lowering of the decomposition of the CHCl_3 and not by any increase in the efficiency for the production of C_2Cl_4 .

Because all the organic products have been measured, the relative amounts of H and Cl atoms appearing as inorganic products can be calculated from the following equations based on mass balance considerations.

$$R(\text{H})_{\text{inorg}} = 2R(\text{C}_2\text{Cl}_4) + R(\text{CCl}_4) + R(\text{CHCl}_3) + 2R(\text{C}_2\text{Cl}_6) - R(\text{CH}_2\text{Cl}_2)$$

$$R(\text{Cl})_{\text{inorg}} = 2R(\text{C}_2\text{Cl}_4) - R(\text{CCl}_4) + R(\text{C}_2\text{HCl}_5) + 2R(\text{C}_2\text{H}_2\text{Cl}_4) + R(\text{CH}_2\text{Cl}_2)$$

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The results of these calculations for the data in Table I and also for data obtained in ^{60}Co irradiations^(2,3) are shown in Table II. For all the experiments other than the nuclear tests, the two values are equal within experimental error, consistent with HCl being the only inorganic product formed with a significant yield. In the results with the nuclear tests there is an excess of H atoms in the inorganic products. Assuming $R(\text{Cl})_{\text{inorg}}$ equals $R(\text{HCl})$ for the nuclear tests, the decrease from the value obtained using the pulsed X-rays is consistent with a decrease in the yield from Reaction 1 [as is the decrease in $R(\text{C}_2\text{HCl}_5)$ and $R(\text{C}_2\text{Cl}_6)$].

Because the 100-eV yield of C_2Cl_4 is independent of dose rates up to a dose rate of approximately 6.4×10^{24} eV/g-sec (1.9×10^3 rads/pulse)⁽³⁾, and also because there are no obvious additional reactions to produce C_2Cl_4 in the nuclear tests, the concentration of this product was used as a measure of the dose received by the samples. For $G(\text{C}_2\text{Cl}_4)$, a value of 0.081 molecule/100-eV was used, the average of the results from References (2), (3) and (6) at room temperature ($\sim 25^\circ\text{C}$). Results of this calculation for the nuclear tests appear in Table II. Earlier results using a nuclear explosion⁽⁸⁾ and the 100-eV yields from other studies^(2,3) are also presented. The 100-eV yields for the nuclear tests appear reasonable in comparison to those obtained with the pulsed X-ray generator⁽³⁾. Values for $G(\text{CCl}_4)$ are higher, while those for $G(\text{C}_2\text{H}_2\text{Cl}_4)$, $G(\text{C}_2\text{HCl}_5)$, and $G(\text{C}_2\text{Cl}_6)$ are all lower. This indicates that no systematic bias is introduced by assuming that $G(\text{C}_2\text{Cl}_4)$ is constant. The changes are also consistent with occurrence of Reactions 8, 9, and 10 which lower the observed values for $G(-\text{CHCl}_3)$.

An "independent action" model, previously developed⁽²⁾ to calculate dose rate effects for product yields in chloroform, has been applied to the data from nuclear tests. In the model, a spur mechanism independent of dose rate is assumed to occur simultaneously with, but independently of, a dose-rate-dependent mechanism involving homogeneously distributed free radicals. Values for the 100-eV yields from the spur mechanism have been determined using Br₂ to scavenge the homogeneously distributed radicals⁽⁶⁾ and NH₃ or n-C₄H₉OH to scavenge positive ions⁽¹²⁾. The products and their 100-eV yields in the spur mechanism⁽⁶⁻¹²⁾ are: C₂H₂Cl₄, 0.34; C₂HCl₅, 0.18; C₂Cl₆, 0.02; and CCl₄, 0.90. The 100-eV yields of CHCl₂ and Cl radicals in the homogeneous mechanism, designated by G(CHCl₂)' and G(Cl)' respectively, can then be calculated by subtracting the spur yields from the measured product yields. The following equations apply.

$$G(Cl)' = 2G(C_2Cl_6) - 2G(C_2Cl_6)_{spur} + G(C_2HCl_5) - G(C_2HCl_5)_{spur} +$$

$$2[G(CCl_4) - G(CCl_4)_{spur}] - G(CH_2Cl_2)$$

$$G(CHCl_2)' = 2G(C_2H_2Cl_4) - 2G(C_2H_2Cl_4)_{spur} + G(C_2HCl_5)$$

$$- G(C_2HCl_5)_{spur} + G(CH_2Cl_2)$$

At dose rates of approximately 6.4×10^{24} eV/g-sec and below, G(CHCl₂)' is 4.1 and G(Cl)' is 3.3 radicals/100-eV⁽³⁾. From the average of the 100-eV yields for the nuclear tests, the calculated values are 3.2 and 2.8, respectively. The uncertainty in each of these values is ± 0.2 based on a 4 to 5% uncertainty in the data in Table II.

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The occurrence of Reaction 9 causes the values for $G(\text{CHCl}_2)'$ and $G(\text{Cl})'$ to be lower than those determined using other radiation sources⁽³⁾. The 100-eV yield of this reaction can be calculated from the difference between the two $G(\text{CHCl}_2)'$ values, $\Delta G(\text{CHCl}_2)$, and also from the difference of the two $G(\text{Cl})'$ values, $\Delta G(\text{Cl})'$, obtained from the different radiation sources. The value of $\Delta G(\text{CHCl}_2)'$ is 0.9; $\Delta G(\text{Cl})'$ is 0.5. The uncertainty in each of these differences is probably ± 0.3 because of the possible errors associated with the calculation of the radical yields. Because these relative uncertainties are large, these two values for $G(9)$ probably can be considered equal, thus consistent with the conclusion that the results can be interpreted with the independent action model⁽²⁾. However, in the calculation for $G(9)$ for each sample the value for $\Delta G(\text{CHCl}_2)'$ was consistently larger than $\Delta G(\text{Cl})'$. This suggests that the difference may indeed be real and indicates the possibility that in the radiolysis with nuclear explosions some process leading to Cl atoms or CCl_3 radicals is occurring without forming CHCl_2 radicals. One possibility is the direct excitation of CHCl_3 to give H atoms and CCl_3 radicals. This may lead to the formation of H_2 and account for the calculated excess of H atoms in the inorganic products. With ^{60}Co gamma rays, Werner and Firestone⁽⁶⁾ have estimated that the 100-eV yield of H atoms is 0.2, but at this dose rate $G(\text{H}_2)$ was only 0.03. The data in Tables II and III suggest that the 100-eV yield for H_2 would be 10 to 20 times larger in irradiations with nuclear explosions.

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Another possibility for the formation of excess CCl_3 radicals is the interaction of the chloroform with the neutrons from the explosion. The most probable interaction would be elastic scattering⁽¹⁶⁾, to produce recoiling hydrogen, carbon, or chlorine ions. The average linear energy transfer (LET) of these species is much higher than that for gamma radiation. This may initiate alternative reactions for the precursors of the radicals⁽⁵⁾, and increase the probability of forming CCl_3 radicals and H atoms. Also the larger LET increases the probability of spur reactions⁽⁵⁾ and could lead to larger 100-eV yields for the products from the spur mechanism. Such an effect would probably be the largest for $G(\text{CCl}_4)_{\text{spur}}$ because it has the largest 100-eV yield of the products formed in the spurs. Any of these factors could account for the small differences calculated for $\Delta G(\text{Cl})'$ and $\Delta G(\text{CHCl}_2)'$. Another effect of the increased spur reactions caused by the high LET resulting from the neutrons would be to lower the 100-eV yield for the total amount of decomposition⁽⁵⁾. This could account for at least part of the decrease in the values of $G(-\text{CHCl}_3)$ observed in the nuclear explosions.

To determine if the high doses/pulse from the nuclear explosion could initiate back reactions for Cl atoms (Reactions 8 and 9) in a homogeneous mechanism, the product yields were calculated with a digital computer. Rate constants chosen for the various reactions are listed in Table IV. Values used for $G(\text{CHCl}_2)'$ and $G(\text{Cl})'$ were 4.1 and 3.3 radicals/100-eV, respectively. The program performed numerical integrations by a fourth-order Runge-Kutta technique⁽¹⁷⁾ and contained a subroutine that simulated the time dependence of

the intensity of a triangular-shaped radiation pulse of variable time width. A comparison of calculated and observed results appears in Table V. The calculated results varied with the dose/pulse but were nearly independent of the time width of the pulse in the range of 10^{-6} to 10^{-8} sec. The results indicate that, at the high dose per pulse from nuclear explosions, recombination reactions involving Cl atoms may occur. At 10^5 rads/pulse, the calculated 100-eV yield for CCl_4 from Reaction 8 in the homogeneous mechanism is 0.12, while at 10^6 rads/pulse it is 0.40. For these same intensities, the calculated values for G(9) are 0.14 and 0.89, respectively, and for G(Cl_2) they are 0.02 and 0.08, respectively. The low values for G(Cl_2) suggest that Reaction 10 is not very efficient and supports the earlier proposal that $R(\text{Cl})_{\text{inorg}}$ is equal to $R(\text{HCl})$ in the results with nuclear explosions. At no dose/pulse was it possible to get complete agreement for all the observed and calculated 100-eV yields. Reasons for the large difference between the values for G(CH_2Cl_2) are not immediately apparent. At least part of the small observed yield of this compound may have originated from the radiolysis at low dose rates caused by the induced radioactivity in the samples, glass ampoules, or secondary containers. At these low dose rates, CH_2Cl_2 is the product having the largest 100-eV yield ($G = 4.1$) since all the CHCl_2 radicals react with CHCl_3 . Considering the uncertainties of some of the above rate constants, and of the shape and quality of the radiation pulse (mixture of gamma rays and neutrons), these calculations serve only to support the hypothesis that back reactions involving the Cl atoms can occur in an homogeneous mechanism in chloroform irradiated with the radiation pulse from a nuclear explosion.


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TABLE I
YIELDS IN THE RADIOLYSIS OF CHLOROFORM
ASSUMING $G(-CHCl_3) = 10.0$ USING VARIOUS SOURCES OF RADIATION

Radiation Source	Relative Product Yields					
	CH_2Cl_2	C_2Cl_4	CCl_4	$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
Nuclear Test 1	0.2	0.10	1.6	1.6	1.7	0.64
"	0.3	0.11	1.8	1.6	1.7	0.57
"	0.3	0.10	1.8	1.4	1.5	0.57
"	0.2	0.10	2.0	1.6	1.6	0.61
Nuclear Test 2	<i>a</i>	<i>a</i>	1.6	1.6	1.8	0.75
"	<i>a</i>	<i>a</i>	1.6	1.6	1.9	0.74
"	<i>a</i>	<i>a</i>	1.6	1.6	1.8	0.75
"	<i>a</i>	<i>a</i>	1.6	1.6	1.8	0.76
Nuclear Test 3	<i>a</i>	<i>a</i>	1.9	1.7	1.7	0.70
"	<i>a</i>	<i>a</i>	1.8	1.6	1.8	0.70
Pulsed X-rays ^b	0.2	0.081	0.98	1.6	1.9	0.89

^aThese values could not be measured accurately due to the low yields of these compounds.

^bReference 3. Average dose rate = $6. \times 10^{24}$ eV/g-sec., $T \approx 25^\circ C$.

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TABLE II
 CALCULATED RELATIVE YIELDS OF H ATOMS AND Cl ATOMS
 IN THE INORGANIC PRODUCTS

<u>Radiation Source</u>	<u>R(H)^a_{inorg}</u>	<u>R(Cl)^a_{inorg}</u>
Nuclear Test 1	4.6	3.7
"	4.6	3.6
"	4.8	3.2
"	4.8	3.2
Pulsed X-rays ^b	4.6	4.5
Cobalt-60 ^c	3.9	3.6
Cobalt-60 ^d	3.8	3.3

^aUncertainties are probably ± 0.3 based on the estimated uncertainties of the measured yields.

^bReference 3. Dose/pulse = 1.9×10^3 rads, $T \approx 25^\circ\text{C}$.

^cReference 3. Dose rate = 1.6×10^{16} eV/g-sec, $T = 25^\circ\text{C}$

^dReference 2. Dose rate = 1.5×10^{15} eV/g-sec, $T = 26^\circ\text{C}$.

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TABLE III
100-eV YIELDS IN THE RADIOLYSIS OF
CHLOROFORM USING VARIOUS RADIATION SOURCES

Radiation Source	100-eV Yields							
	HCl	CH ₂ Cl ₂	C ₂ Cl ₄	CCl ₄	C ₂ H ₂ Cl ₄	C ₂ HCl ₅	C ₂ Cl ₆	-CHCl ₃ ^a
Nuclear Test ^b								
1	3.0 ^c	0.3	<i>d</i>	1.3	1.3	1.4	0.51	8.2
1	2.7 ^c	0.2	<i>d</i>	1.3	1.2	1.2	0.40	7.1
1	2.6 ^c	0.2	<i>d</i>	1.5	1.2	1.4	0.49	8.0
1	2.6 ^c	0.2	<i>d</i>	1.6	1.3	1.3	0.48	8.1
Average ^e	2.7	0.2	<i>d</i>	1.4	1.3	1.3	0.47	7.8
Nuclear Test ^f	<i>g</i>	0.07	<i>d</i>	<i>g</i>	1.2	1.0	0.31	<i>e</i>
Pulsed X-rays ^h	4.5 ⁱ	0.2	0.078	0.94	1.5	1.8	0.85	9.6
⁶⁰ Co γ-rays ^j	4.2	1.9	0.085	0.89	0.73	1.6	2.0	11.6
⁶⁰ Co γ-rays ^k	4.4	2.7	0.074	0.8	0.53	0.88	2.8	12.1

^aCalculated from organic product yields.

^bCalculated assuming $G(\text{C}_2\text{Cl}_4) = 0.081$, dose/pulse $\cong 10^5 - 10^6$ rads.

^cAssumed equal to $G(\text{Cl})_{\text{inorg}}$ calculated from the mass balance equations.

^dAssumed to be 0.081.

^eThe results of tests in which CH₂Cl₂ and C₂Cl₄ could not be measured accurately are not included in this average. However, if 100-eV yields are calculated for the measured products in these tests by assuming that either $G(\text{C}_2\text{H}_2\text{Cl}_4)$ or $G(\text{C}_2\text{HCl}_5)$ equals 1.3, the results differ by 0.1 unit or less from the averages in the Table.

^fReference 8. Calculated assuming $G(\text{C}_2\text{Cl}_4) = 0.081$.

^gNot determined.

^hReference 3. Dose/pulse = 1.9×10^3 rads, $T \cong 25^\circ\text{C}$.

ⁱAverage value of $G(\text{Cl})_{\text{inorg}}$ and $G(\text{H})_{\text{inorg}}$.

^jReference 3. Dose rate = 1.6×10^{16} eV/g-sec, $T = 25^\circ\text{C}$.

^kReference 2. Dose rate = 1.5×10^{15} eV/g-sec, $T = 26^\circ\text{C}$.

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TABLE IV
 RATE CONSTANTS USED IN THE COMPUTER
 CALCULATION OF PRODUCT YIELDS

<u>Reaction No.</u>	<u>Rate Constant (M⁻¹ sec⁻¹)</u>	<u>Source</u>
1	1.1 x 10 ⁷	Reference 18
2	1.1	Reference 2
3	5.0 x 10 ⁷	Reference 2
4	7.5 x 10 ⁷	Reference 2
5	5.0 x 10 ⁷	Reference 19
8	2.0 x 10 ¹⁰	<i>a</i>
9	2.0 x 10 ¹⁰	<i>a</i>
10	1.3 x 10 ¹⁰	<i>a</i>

a. Calculated from the modified equation assuming the reaction to be diffusion controlled. Reference 20.

TABLE V
COMPARISONS OF OBSERVED AND CALCULATED
100-eV YIELDS IN THE RADIOLYSIS OF CHLOROFORM USING
A NUCLEAR EXPLOSION

Product	100-eV Yields			
	Observed	Calculated ^a		
		1×10^5 rads/pulse	5×10^5 rads/pulse	1×10^6 rads/pulse
CH ₂ Cl ₂	0.2	0.0030	0.0007	0.0003
CCl ₄	1.4	1.0	1.2	1.3
C ₂ H ₂ Cl ₄	1.3	1.6	1.5	1.5
C ₂ HCl ₅	1.3	1.6	1.3	1.1
C ₂ Cl ₆	0.46	0.73	0.47	0.29
Reaction 9 ^b	0.9	0.1	0.5	0.9
HCl	2.7 ^c	3.0	2.4	1.9

^aSum of the 100-eV yields for the spur mechanisms and those calculated for the homogeneous mechanism at various doses per pulse and a pulse width of 7×10^{-9} sec.

^b100-eV yield of the recombination of CHCl₂ and Cl radicals.

^cCalculated from mass balance equations.

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