View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

Radiolysis of Vinyl Iodide

Part 2.—Solutions of Vinyl Iodide in Carbon Tetrachloride

By Pierre C. Roberge * and Jan A. Herman

Dept. of Chemistry, Laval University, Quebec, P.Q., Canada

Received 21*st May*, 1968

Radiolysis of solutions of vinyl iodide in carbon tetrachloride enables a mechanism of formation of products to be specified. Ethylene is formed within spurs in reactions involving vinyl radicals and hydrogen iodide, while acetylene is formed in three different processes involving molecular decomposition of vinyl iodide, and hydrogen-abstraction reactions by either iodide or chlorine atoms from vinyl radicals. Hydrogen iodide is formed in hydrogen-abstraction reaction by atomic iodine from vinyl radical. Hydrogen is formed in the molecular decomposition and by hot hydrogen atom abstraction. Hydrogen chloride is formed mainly by hot chlorine atom abstraction of hydrogen from vinyl iodide. Competition between the dissociative electron attachment processes of CCl_4 and C_2H_3I strongly affects the hydrogen chloride formation. Vinyl chloride is formed within spurs in reactions involving vinyl radicals and HCl or Cl atoms. There is no evidence of electronic excitation transfer in the present system, and charge transfer seems improbable.

We have studied the radiolysis of pure liquid vinyl iodide.[1] The formation of radical scavengers, iodine and hydrogen iodide (total yield = 3·1 molecules/100 eV), prevents any bulk polymerization of the pure vinyl iodide. Diffusion-controlled radical reactions within the spurs have been postulated as responsible for most of the products formed during radiolysis. We extended the previous investigations to solutions of vinyl iodide in carbon tetrachloride. In such solutions, iodine and hydrogen iodide formation being inhibited, polymerization readily occurs. The polymerization processes will be specifically examined in a separate paper. The present work is devoted to the study of the formation of different gaseous products as a function of vinyl iodide concentration in order to check the radiolytical processes already suggested.[1]

EXPERIMENTAL

The experimental procedures are described elsewhere.[1-3] We shall recall only the essential features. Vinyl iodide was prepared by the method of Spence,[4] and after careful purification, the monomer contained less than 0·01 % impurities, as shown by gas chromatography. The carbon tetrachloride, Research Grade, was distilled under vacuum ($>10^{-5}$ torr) through a mixture of magnesium sulphate and soda lime in order to free it from traces of water, hydrochloric acid and oxygen. Both compounds were kept in the dark and under high vacuum.

The solutions were prepared under vacuum by mixing weighed (precision better than 0·5 %), or volumetrically measured (precision ±5 %), quantities of the components. All samples were sealed in Pyrex cells (volume 5 ml) equipped with break seals. Irradiation was carried out in the Gamma-cell 200 (A.E.C.L.) irradiator at room temperature at a dose-rate of $2{\cdot}8\times10^5$ rad/h. Some irradiations were performed at lower dose-rate. Yields are reported relative to $G = 15{\cdot}6$ for the Fricke dosimeter, but corrections were

* present address : Laboratoire de Photophysique Moleculaire, Faculté des Sciences, Orsay, France.

View Article Online

made for the low-energy components in the cylindrical Co^{60} source, which causes a significant increase of the energy absorbed by the iodine atoms.[5] These corrections which apply only to vinyl iodide, were established relative to $G(I_2) = 2{\cdot}07$ in pure liquid ethyl iodide.[6-8] The total doses absorbed varied from 10^{19} to 20×10^{19} eV/ml of solution.

Gaseous products were analyzed by G.C.; iodine was measured by spectrophotometry at 500 nm. Hydrogen chloride and hydrogen iodide were extracted by water following irradiation, and these aqueous solution titrated; HI was estimated by spectrophotometry at 226 nm, and the sum of HCl and HI by acidimetry.

RESULTS

Radiolysis of vinyl iodide in carbon tetrachloride solutions yielded the following products: H_2, C_2H_2, C_2H_4, C_4H_6, HI, I_2, HCl, C_2H_3Cl, CH_3Cl and the polymer. At high concentration of vinyl iodide (80 M %), a non-identified product appeared which seems to be related to the formation of molecular iodine or hydrogen iodide in solution.

The amounts of H_2, C_2H_2, C_2H_4, C_4H_6, HI, HCl and the polymer produced, are linear with the absorbed dose, at least for doses not exceeding 3×10^{19} eV/ml. For prolonged irradiation (absorbed doses up to $1{\cdot}2 \times 10^{20}$ eV/ml) the production of H_2 is still linear, but the rates of formation of C_2H_4 and C_2H_2 decrease slightly (*ca.* 20 % at the highest absorbed dose). The rate of molecular iodine formation decreases with increase of absorbed doses, suggesting the occurrence of secondary reactions involving iodine consumption. This effect is more pronounced in the radiolysis of pure vinyl iodide.[1] The rate of formation of C_2H_3Cl and CH_3Cl decrease even more rapidly than that of iodine. The reduced rates of formation of C_2H_2, C_2H_4 and C_2H_3Cl for prolonged irradiations cannot be ascribed to the accumulation of radical scavengers in the system, since the formation of these products is only slightly affected by the addition of large quantities of radical scavengers. Copolymerization of these different unsaturated compounds seems more plausible explanation of their behaviour at high absorbed doses.

The *G* values of products as a function of vinyl iodide concentration (in mole %), are presented in fig. 1-4. The iodine formation starts at a vinyl iodide concentration of about 80 mole % and this coincides with the disappearance of polymerization in the solution (fig. 3). The HI production also increases sharply at the same time as molecular iodine appears in solutions. The radiochemical yields obtained at different dose-rates are given in table 1. The formation of the different products, at least for iodide concentration lower than 50 mole %, is not affected or slightly so by a change of the radiation intensity. A similar independence of the yields with the dose-rate was noted in the radiolysis of pure vinyl iodide.[1] Addition of oxygen to the system does not affect significantly the formation of C_2H_4, H_2, C_4H_6, and C_2H_3Cl, while CH_3Cl formation is strongly inhibited (table 1). The results for C_2H_2 in the presence of O_2 are meaningless, thermal (and may be radiolytical) oxidation of C_2H_3I giving C_2H_2 as a product.[3]. Addition of HCl causes the C_2H_3Cl and C_2H_4 yields to increase markedly, while the C_2H_2 yield decreases. With the exception of the polymer,[9] we did not identify any molecular species derived from the $CCl_3\cdot$ radical, the lack of an efficient analytical procedure being the main reason.

DISCUSSION

Previously we conclude that most of the main products are formed within spurs in diffusion-controlled processes [1]; this conclusion was based on the small intensity effect and on the slight action of radical scavenger (DPPH) on the formation of the products. Such diffusion-controlled processes have been invoked by Gillis [10] and

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

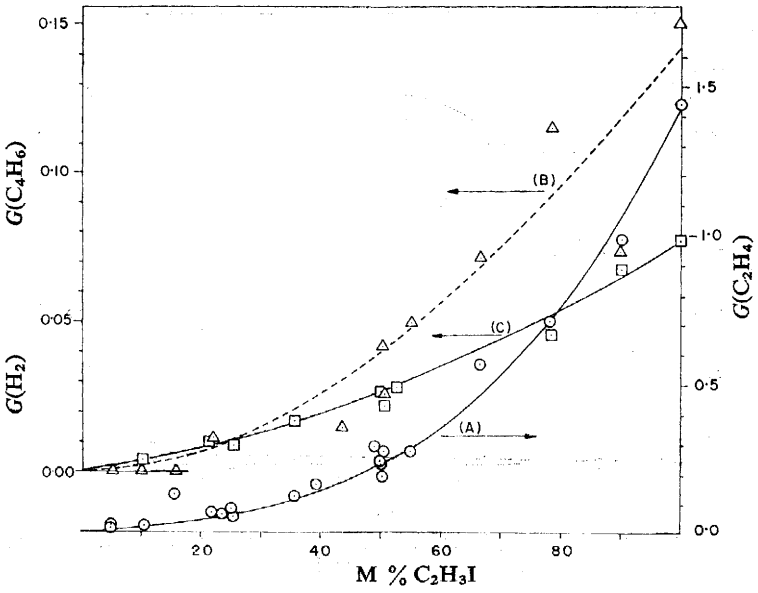

FIG. 1.—Yields of ethylene (○), butadiene (△) and hydrogen (□), as a function of vinyl iodide concentration in mole %.

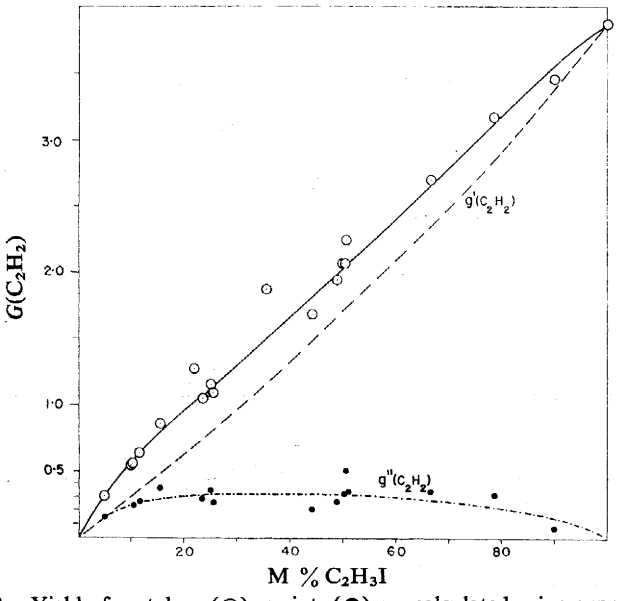

FIG. 2.—Yield of acetylene (○); points (●) are calculated using expression (*d*).

Schindler [6] to explain the radiolysis of liquid ethyl iodide. In the present case the above hypothesis is roughly confirmed.

The formation of radiolysis products might be partly explained by the following sequence of reactions. Species taking part in diffusion-controlled processes within the spur are enclosed in parentheses.

$$n\ C_2H_3I,\ m\ CCl_4 \overset{\gamma}{\rightsquigarrow} (n\ C_2H_3 + n\ I + m\ CCl_3 + m\ Cl), \qquad (1)$$

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

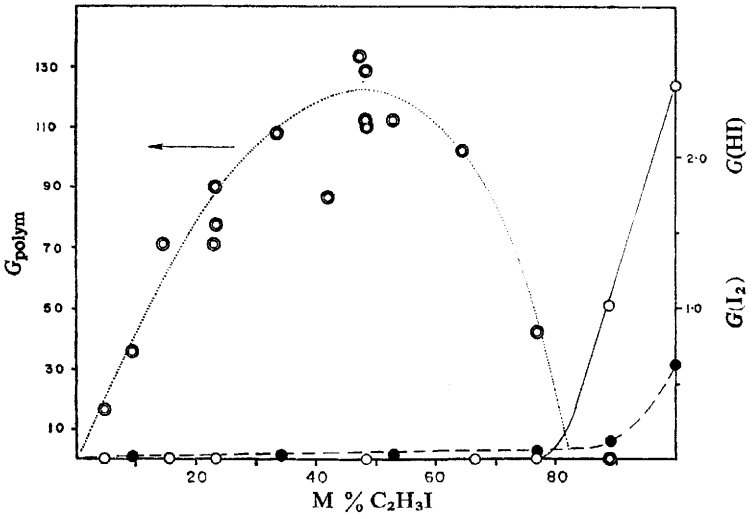

FIG. 3.—Yields of molecular iodine (○), hydrogen iodide (●) and polymer (◎), as a function of vinyl iodide concentration in mole %.

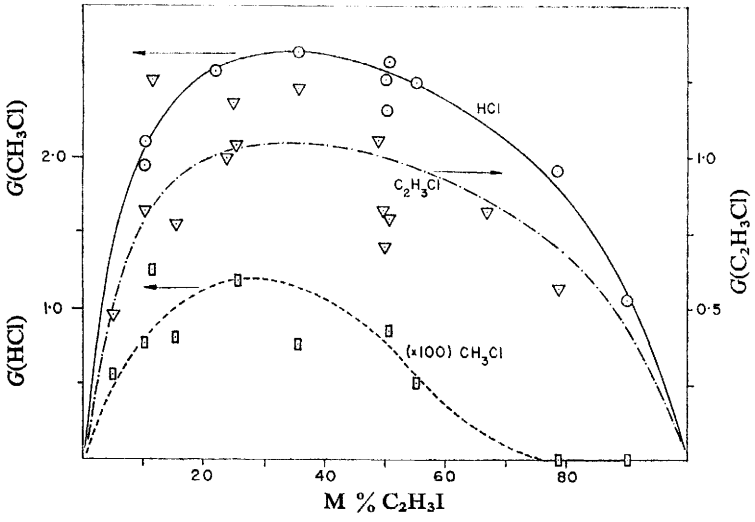

FIG. 4.—Yields of hydrogen chloride (○), vinyl chloride (▽) and methyl chloride (□), as a function of vinyl iodide concentration in mole %.

where n and m are small integers. The intraspur fragments, upon encounter, can either recombine or disproportionate, or can diffuse outside the spur. For the sake of clarity, we omit all recombination reactions leading to the initial reactants,

$$(2\,C_2H_3+2\,I)\rightarrow C_2H_2+(C_2H_3+HI+I) \quad (2)$$

$$(C_2H_3+C_2H_3)\rightarrow C_4H_6 \quad (3)$$

$$(C_2H_3+Cl)\rightarrow C_2H_2+HCl \quad (4)$$

$$\rightarrow C_2H_3Cl \quad (5)$$

$$(I+I)\rightarrow I_2 \quad (6)$$

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

An efficient reaction occurs between $C_2H_3\cdot$ and HI,[3, 11] and therefore, we must include, as a second-stage spur reaction following step (2), the reaction (7) and (2*a*):

$$(C_2H_3+HI+I)\rightarrow C_2H_4+(I+I) \quad (7)$$

$$\rightarrow n\ HI+\text{either } C_2H_2 \text{ or } C_2H_3I. \quad (2a)$$

The radicals may also react with the cage. Reaction (8) has already been evidenced by photolysis [3]:

$$(C_2H_3+CCl_4)\rightarrow C_2H_3Cl+CCl_3\cdot.$$

Chlorine atoms may either add to the double bond of the vinyl iodide or abstract a hydrogen atom:

$$(Cl+C_2H_3I)\rightarrow(C_2H_3ICl\cdot) \quad (9)$$

$$\rightarrow HCl+(C_2H_2I\cdot). \quad (10)$$

Reaction (10) is followed by

$$(C_2H_2I+R)\rightarrow C_2H_2+RI, \quad (11)$$

where R might be any radical.

One expects that similar intraspur processes between CCl_3 and Cl fragments and other radicals might take place leading to the formation of such products as Cl_2, C_2Cl_6,[12, 13] or ICl, $ClCl_3$ $CHCl_3$, $C_2H_3Cl_3$, etc. However, we failed to identify these products.

If the fragments diffuse outside the spurs, they can undergo reactions similar to those already described, but they can be differentiated from the above by their sensitivity to radical scavengers and they should display a dose-rate effect.

FORMATION OF ETHYLENE

If $G_v(C_2H_4)$ is the number of ethylene molecules formed for 100 eV absorbed by *vinyl iodide only*, then it can be represented as a function of the monomer concentration (in mole/l.) by the following expression:

$$G_v(C_2H_4) = 0{\cdot}114+7{\cdot}705\times10^{-3}\,[C_2H_3I]^2. \quad (a)$$

Consequently, the formation of ethylene as a function of the absorbed dose may be represented by the following analytical expression:

$$[C_2H_4] = A[C_2H_3I]+B[C_2H_3I]^3, \quad (b)$$

where A and B are numerical constants taking into account the absorbed dose during the time, t. Curve A in fig. 1 has been computed according to expression (*a*), allowance being made for the total energy absorbed by the systems; the points are experimental. Eqn. (*b*) indicates the existence of at least two distinct processes leading to C_2H_4 formation.

The most important process with a G value of 1·33 for the pure vinyl iodide, is characterized by a cubic dependence on C_2H_3I concentration. On consideration of the primary step (1) and reaction (7), it follows that the HI concentration in the spurs increases as the square of the C_2H_3I concentration, while the concentration of vinyl is directly proportional to the iodide concentration. Therefore, the rate of formation of ethylene will vary as the cube of the monomer concentration, as experimentally found. However, there is a small decrease of the $[C_2H_4]$ formed in the presence of added oxygen (table 1) and DPPH,[1] which suggests the occurrence of the following reaction outside the spurs:

$$C_2H_3\cdot+HI\rightarrow C_2H_4+I\cdot. \quad (7a)$$

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

TABLE 1

C_2H_3I mole %	relative intensity	additives	$G(H_2)$	$G(C_2H_2)$	$G(C_2H_4)$	$G(C_4H_6)$	$G(HI)$	$G(HCl)$	$G(C_2H_3Cl)$	$G(CH_3Cl)$
10·3	1	—	0·004	0·56	0·011	—	0·02	1·94	0·83	0·008
10·3	1/8	—	0·004	0·55	0·010	—	0·03	2·10	0·59	0·005
21·7	1	—	0·007	1·04	0·06	0·006	—	(2·45)†	(1·07)†	—
21·7	1/3	—	0·009	1·27	0·07	0·012	0·01	2·57	0·83	—
50·5	1	—	0·026	2·16	0·22	0·04	0·06	2·59	(1·0)†	0·009
50·5	1/8	—	0·022	1·74	0·19	0·04	0·04	2·30	0·77	0·005
65·7	1	—	0·039	2·60	0·45	0·07	—	(2·32)†	0·83	(0·004)†
65·7	1	oxygen (0·03 mole/l.)	0·036		0·39	0·08	—	—	0·86	0·001
65·7	1	HCl (0·13 mole/l.)	0·036	2·25	0·93	0·07	0·04	—	1·21	0·003
100*	1	—	0·077	3·89	1·46	0·15	0·63	—	—	—

* mean from 4 experiments; † intrapolated from fig. 4

Experiments at 65·7 mole % of C_2H_3I in the presence of O_2 (table 1) and in pure monomer in the presence of DPPH indicate that reaction (7) is approximately 4 times as probable as reaction (7*a*).

The second process of C_2H_4 formation is characterized by a first-order dependence upon vinyl iodide concentration. With a G value of 0·1, it does not contribute more than about 8 % to the total ethylene yield in pure vinyl iodide; however, it becomes the main source of C_2H_4 at low monomer concentration. This process cannot be a one-act process.

Hydrogen atoms are removed from the system by addition to the double bond ($g(H)_{add} = 1{\cdot}8$ in pure C_2H_3I)[1];

$$H\cdot + C_2H_3I \rightarrow C_2H_4I\cdot. \qquad (12)$$

The $C_2H_4I\cdot$ radical so formed can disproportionate with any radical R· to give C_2H_4:

$$C_2H_4I\cdot + R\cdot \rightarrow C_2H_4 + RI. \qquad (13)$$

The sequence of reactions (12) and (13) will lead to the observed first-order dependence of ethylene on vinyl iodide concentration provided two conditions are fulfilled: (*a*) vinyl iodide is an efficient hydrogen atoms scavenger, in which case low concentrations of the monomer will intercept all the hydrogen atoms produced. This condition should be fulfilled. (*b*) $C_2H_4I\cdot$ radicals do not add efficiently to vinyl iodide. In view of the low reactivity of vinyl radicals towards the double bond of vinyl iodide,[3, 11] this second condition is likely to be met.

Using ($gC_2H_4I\cdot$) = 1·8 for $C_2H_4I\cdot$ radicals in pure vinyl iodide (which is the G value of scavenged hydrogen atoms), and $G'(C_2H_4) = 0{\cdot}114$ (first-order process of C_2H_4 formation), we calculate a minimum value of the disproportionation to recombination ratio, $k_{13}/k_{14} = 0{\cdot}06$,

$$C_2H_4I\cdot + R\cdot \rightarrow C_2H_4IR. \qquad (14)$$

The addition of large quantities of HCl to the system enhances the formation of C_2H_4 (table 1), suggesting the occurrence of the reaction:

$$C_2H_3\cdot + HCl \rightarrow C_2H_4 + Cl\cdot. \qquad (15)$$

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

This reaction was postulated by Hupin [14] to account for the effect of HCl in the radiolysis of gaseous C_2H_3Cl. With reference to the heat of formation of the vinyl radical,[15] the reaction (15) would be slightly exothermic (*ca.* -2 kcal/mole), but its activation energy is unknown. From the magnitude of the increase of C_2H_4 caused by the addition of HCl we conclude that the contribution of reaction (15) is negligible and accounts for no more than 5 % to the total $G(C_2H_4)$. The contribution of the same reaction occurring within the spur should be even smaller.

FORMATION OF ACETYLENE

The fact that the C_2H_2 yield is not greatly affected by a change in dose-rate (table 1) or by the presence of radical scavengers,[1] implies that acetylene is formed in the decomposition of excited or ionized vinyl iodide molecules, or that it is the product of intraspur radical reactions. We have presented evidence [1] for the following processes: (*a*) decomposition reactions ($G_{16,17} = 1{\cdot}80$):

$$C_2H_3I^* \rightarrow C_2H_2 + H + I \tag{16}$$

$$C_2H_3I^+ \rightarrow C_2H_2 + H + I^+. \tag{17}$$

(*b*) hydrogen-abstraction reactions (2, 2*a*). The latter account for $G_{C_2H_2,\,\mathrm{dispr}} = 2{\cdot}09$ in pure vinyl iodide.[1]

The contribution of both processes, as expressed by their corresponding yields, $g'(C_2H_2) = G_{16,17} + G_{C_2H_2,\mathrm{dispr}}$, is plotted (dashed line) as a function of the monomer concentration in fig. 2. The difference between the experimental (full line) and calculated yields,

$$g''(C_2H_2) = G(C_2H_2) - g'(C_2H_2),$$

reflects the existence of a third mechanism of acetylene formation in CCl_4 solutions. In fig. 2 the curve g'' has been plotted according to $g''(C_2H_2) = 0{\cdot}125\ G(\mathrm{HCl})$, while the points are experimentally deduced from the expression (*c*); the fit is satisfactory. That means, that reactions (4) can account for no more than 12 % of the HCl formation.

On the other hand, the addition of HCl to the system decreases the quantity of acetylene formed and at the same time an increase of the vinyl chloride is noted (table 1). The concentration of added HCl is much too low (considering its low efficiency as a radical scavenger) to compete with processes occuring within the spurs. Consequently, a non-negligible quantity of C_2H_2 formed must come from a reaction occurring in the stationary state (as distinct from spurs). The present results (fig. 2) would indicate that the totality of the C_2H_2 formed by the third mechanism is produced in the stationary state. However, due to lack of precision of $g''(C_2H_2)$, a systematic study of the HCl effect would be necessary to proceed further.,

FORMATION OF 1,3-BUTADIENE AND HYDROGEN

The formation of butadiene is not influenced by the presence of radical scavengers, nor does it show any dose-rate effect (table 1). The result can be fitted by the experimental expression (curve B in fig. 1):

$$G_v(C_4H_6) = 1{\cdot}09 \times 10^{-2}[C_2H_3I], \tag{d}$$

where G_v (product) is the yield for 100 eV of energy absorbed solely by C_2H_3I, and the concentration of the monomer is expressed in mole/l. This expression implies that the rate of formation of C_4H_6 varies as the square of the vinyl iodide concentration. We have already assumed [1] that butadiene is formed by diffusion-controlled

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

recombination of vinyl radicals within the spurs (reaction (3)), and such process is consistent with the present results.

We have shown the fast removal of hydrogen atoms by addition to the double bond of vinyl iodide,[1] $g(H)_{add} = 1{\cdot}8$. This means that the hydrogen observed is formed by molecular elimination, ion-molecule reaction or hot atom reaction. Hydrogen formation is well described by the following expression:

$$G_v(H_2) = 0{\cdot}017 + 4{\cdot}5 \times 10^{-3}[C_2H_3I]. \qquad (e)$$

Curve C in fig. 1 has been computed according to this expression, and then related to the total absorbed dose. Eqn. (*e*) indicates that at least two distinct processes are involved: (*a*) the first, with a $G'(H_2) = 0{\cdot}017$ for pure vinyl iodide, is characterized by a first-order dependence on the monomer concentration. Molecular elimination of hydrogen from a highly excited or superexcited state,[16] as well as from an ion, constitutes the most likely mechanism for this process:

$$C_2H_3I^* \rightarrow H_2 + C_2HI \qquad (18)$$

$$C_2H_3I^+ \rightarrow H_2 + (\text{fragments})^+. \qquad (19)$$

(*b*) The second mode of formation of H_2, with a $G''(H_2) = 0{\cdot}059$ in pure vinyl iodide, shows a second-order dependence on monomer concentration. Hydrogen abstraction by hot hydrogen atoms

$$H\cdot + C_2H_3I \rightarrow H_2 + C_2H_2I\cdot \qquad (20)$$

is a conceivable explanation of the observed yield, $G''(H_2)$.

FORMATION OF HYDROGEN IODIDE AND IODINE

HI is entirely formed by the hydrogen-abstraction reactions (2) and (2*a*). This is evidenced by the third order dependence of the rate of C_2H_4 formation upon the vinyl iodide concentration, as well as by the material balancing of HI formation in pure vinyl iodide.[1] Molecular iodine can only be formed by recombination of iodide atoms, and this process can take place inside (reaction (6)), as well as outside, the spurs.

The production of both HI and I_2 is strongly inhibited in CCl_4 solutions (fig. 3). When both products appear in significant amounts, at vinyl concentration of about 80 mole %, the rate of polymerization drops abruptly. However, the iodine atoms are released in reactions (2), (2*a*), (7), (7*a*) and material balancing requires, that the rate of iodine formation is

$$v_{I_2} \geqslant \tfrac{1}{2}[v_2^{C_2H_2} + v_{2a}^{C_2H_2} + v_7^{C_2H_4} + v_{7a}^{C_2H_4}];$$

hence, there should be a substancial yield of I_2 (greater than that of $G_{C_2H_2,\text{dispr}\cdot}$) over the whole range of vinyl iodide concentrations. Therefore, the protection against the accumulation of HI or I_2 in solution must be attributed to intraspur or extraspur processes involving reactions with the solvent radicals:

$$CCl_3\cdot + I\cdot \rightarrow CCl_3I \qquad (21)$$

$$CCl_3\cdot + HI \rightarrow CHCl_3 + I\cdot \qquad (22)$$

$$Cl\cdot + I\cdot \rightarrow ICl \qquad (23)$$

$$Cl\cdot + HI \rightarrow HCl + I\cdot \qquad (24)$$

With the exception of hydrogen chloride, none of these products could be positively identified. However, West[17] reported, that in gamma-irradiated $CHCl_3 + C_2H_5I$ mixtures there is formation of trichloroiodomethane; we think that a similar reaction

View Article Online

take place in the present system. On the other hand, some experiments carried on in this laboratory on the radiolysis of iodine in pure CCl_4 [18] give a high yield of iodine disappearance, ($G(-I_2) \simeq 17$). This confirms that ICl and/or CCl_3I are stable enough to explain the protection against iodine accumulation in the $CCl_4 + C_2H_3I$ system.

FORMATION OF HYDROGEN CHLORIDE

The HCl formed in reaction (4) (or in a similar extraspur reaction) can account for no more than 12 % of HCl formation. Reaction (25),

$$H\cdot + CCl_4 \rightarrow HCl + CCl_3\cdot \tag{25}$$

which has been suggested [19] could only be important at high CCl_4 concentration, since C_2H_3I is an efficient scavenger of hydrogen atoms.[1] At a CCl_4 concentration of 90 mole %, the 100 eV yield of hydrogen atoms is 0·2 and reaction (25) contributes no more than 10 % of the total HCl formation at low vinyl iodide concentration.

Reaction (10) must then constitute the main source of HCl. It may occur inside as well as outside of the spurs. Bellas *et al.*[20] determined the activation energy of reaction (26):

$$Cl\cdot + C_2H_3Cl \rightarrow HCl + C_2H_2Cl\cdot \tag{26}$$

as 16·0 kcal/mole in the gas phase. The activation energies of reactions (26) and (10) should not be very different and the importance of reaction (10) in the radiolysis implies that chlorine atoms are produced with a high translational energy. These " hot " Cl atoms may arise from decomposition of an excited (or superexcited) state of CCl_4, as well as from the neutralization of Cl^- (or CCl_4^-) which is formed by dissociative attachment of thermalized electrons by CCl_4.[21] An activation energy of 20 kcal/mole [22, 23] has been attributed to gas phase reaction (27):

$$Cl\cdot + CCl_4 \rightarrow Cl_2 + CCl_3\cdot, \tag{27}$$

and therefore it will compete with reaction (10).

If the concentration of hot Cl atoms is proportional to the CCl_4 concentration, we can obtain the fraction of these $\underline{Cl}$ atoms (f_{Cl}) that have reacted according to reaction (10) in order to reproduce the observed HCl production (fig. 4). The curve of the fraction of $\underline{Cl}$ atoms so calculated (curve 1) is given in fig. 5. There are two inflexion points, thus indicating that the concentration of hot Cl atoms is not directly proportional to CCl_3 concentration. Carbon tetrachloride has a higher electron capture cross-section than iodides.[24, 25] As neutralization of Cl^- ions will lead to Cl atoms formation,[26] the competition between dissociative electron attachment processes (28) and (29),

$$C_2H_3I + e^- \rightarrow C_2H_3 + I^- \tag{28}$$

$$CCl_4 + e^- \rightarrow CCl_3 + Cl^-, \tag{29}$$

has to be taken into account when evaluating the relative chlorine atom concentration. Assuming the radiochemical yield of electrons in C_2H_3I as 3·5, we calculated f_{Cl} curves for different values of $g(\underline{Cl}\cdot)$ (for pure CCl_4) and different ratio k_{29}/k_{28}. Some of these curves are plotted in fig. 5. The f_{Cl} curves become monotonic for a value $k_{29}/k_{28} = 4$, for any value of $g(\underline{Cl}\cdot)$ used.

In the simplest case where reaction (27) is the only one to compete with reaction (10) for hot $\underline{Cl}$ atoms,

$$f_{Cl} = \frac{k_{10}[C_2H_3I]}{k_{27}[CCl_4] + k_{10}[C_2H_3I]} \tag{f}$$

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

View Article Online

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

Using the empirical expression,[11]

$$[CCl_4] = 10{\cdot}3 - 0{\cdot}78[C_2H_3I],$$

where the concentrations are in mole/l., expression (f) becomes

$$(f_{Cl})^{-1} = 1 - 0{\cdot}78k_{27}/k_{10} + 10{\cdot}3\,(k_{27}/k_{10})\,[C_2H_3I]^{-1}. \qquad (g)$$

Values of $(f_{Cl})^{-1}$ obtained from curves 5 and 6 of fig. 5 (with $k_{29}/k_{28} = 4$) are plotted as a function of the reciprocal C_2H_3I concentration. Fig. 6 shows that relation (g)

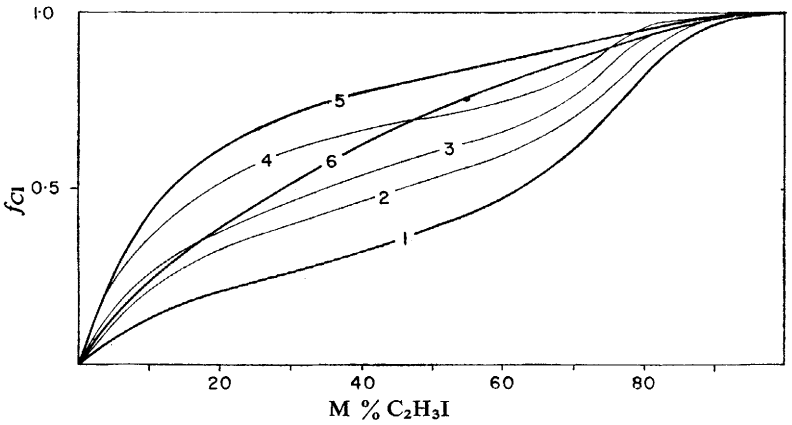

FIG. 5.—Fraction of hot chlorine atoms utilized in reaction (10). Calculated for the following conditions: curve 1, $[Cl\cdot] \propto [CCl_4]$; curve 2, $k_{29}/k_{28} = 2, g(Cl\cdot) = 9$; curve 3, $k_{29}/k_{28} = 3$, $g(Cl\cdot) = 9$; curve 4, $k_{29}/k_{28} = 3$, $g(Cl\cdot) = 5$; curve 5, $k_{29}/k_{28} = 4$, $g(Cl\cdot) = 4$; curve 6, $k_{29}/k_{28} = 4$, $g(Cl\cdot) = 9$.

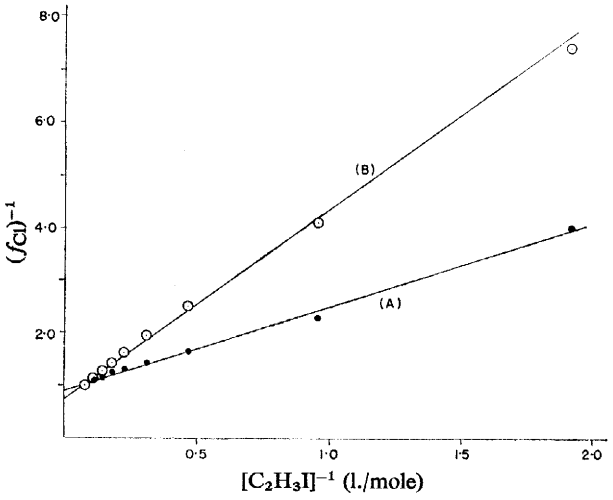

FIG. 6.—Reciprocal of f_{Cl} as function of the reciprocal of vinyl iodide concentration according to relation (g).

applies satisfactorily. For f_{Cl} values calculated with g (Cl·) = 4, (curve 5 of fig. 5), the k_{27}/k_{10} ratios are respectively, 0·13 or 0·15, when calculated from the intercept and the slope of the straight line A, fig. 6. For f_{Cl} values calculated with $g(Cl\cdot) = 9$, (curve 6 in fig. 5), the values of k_{27}/k_{10} are 0·32 and 0·34, respectively (line B in fig. 6). Although the value of $g(Cl\cdot)$ is not critical for the evaluation of the k_{29}/k_{28} ratio, it

View Article Online

is essential for a precise determination of the rate-constant ratio k_{27}/k_{10}. The 100 eV yield for radicals in CCl_4 is uncertain, as it depends on the method used for its measurements; published values vary from 7 to 18.[12, 18, 27-30] Even if it known precisely, it would only permit an evaluation of the upper limit of the radiochemical yield of hot chlorine atoms. On the other hand, the preceding discussion showed the importance of the electron capture by CCl_4 on the formation HCl. If we attribute a lower limit of 3 to $g(Cl\cdot)$, consequently, the ratio $k_{27}/k_{10} = 0{\cdot}2 \pm 0{\cdot}1$, which is consistent with the activation energies of 20 and 16 kcal/mole for reactions (27) and (10) respectively.

FORMATION OF VINYL CHLORIDE

Vinyl chloride is mainly formed via spur reactions as shown by its insensitivity to the presence of radical scavengers (table 1). Three main spur processes leading to C_2H_3Cl formation need to be considered: reactions (5), (9), (30) [and to a lesser extent reaction (8)]:

$$(HCl + C_2H_2I\cdot) \rightarrow (C_2H_3ICl)^* \begin{cases} \nearrow C_2H_3Cl + I\cdot & (30) \\ \searrow C_2H_3I + Cl\cdot. & (30a) \end{cases}$$

Reactions analogous to (30), and (9) have been postulated by Bellas *et al.*[20] in their study of the Hg photosensitization of vinyl chloride. The experimental results for C_2H_3Cl formation can be fitted satisfactorily the expression (see fig. 4):

$$G(C_2H_3Cl) = 0{\cdot}394\ G(HCl).$$

This behaviour is consistent with any of the three processes. However, our results do not permit an evaluation of the relative contributions of these different processes. A consideration of the collision frequency in $CCl_4 + C_2H_3I$ mixtures gives an upper limit of 10^{-12} sec for lifetime of $(C_2H_3ICl)^*$ species, if process (9) and (30) are operative.

CONCLUDING REMARKS

The present data do not show any evidence of electronic excitation transfer in the system $CCl_4 + C_2H_3I$ (nor of charge transfer). However, the study of the chlorinated products indicates the importance of dissociative electron attachment in the radiolysis of $CCl_4 + C_2H_3I$ mixtures. We calculate that CCl_4 is four times more efficient than C_2H_3I as an electron captor. Frankevich[25] gives CCl_4 as 2 times more efficient than CH_3I and HI, and 3·3 times more efficient than C_2H_5I. Considering that the C—I bond is stronger in C_2H_3I than in C_2H_5I due to electron delocalization, our value of 4 is consistent with Frankevich's data. Dissociative capture of an electron giving $C_2H_3 + I^-$ or $CCl_3 + Cl^-$ followed by migration of I^- or Cl^- in the coulombic field of a positive ion, would eventually leave C_2H_3 and I, or CCl_3 and Cl, well separated. The C_2H_3 and CCl_3 radicals so produced will be mainly located outside of the spurs. On the other hand, the neutralization proces will yield Cl or I atoms located inside of a cage (or a spur):

$$M^+ + X^- \rightarrow (M\cdot + X\cdot),$$

where X stands for Cl or I. Consequently, the competition between CCl_4 and C_2H_3I for electron attachment will mainly affect the formation of the chlorinated products.

This work was made possible through the financial assistance of the National Research Council of Canada.

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.

View Article Online

[1] J. A. Herman and P. C. Roberge, *Trans. Faraday Soc.*, 1966, **62,** 3183.
[2] J. A. Herman and P. C. Roberge, *J. Polymer Sci.*, 1962, **62,** S-116.
[3] P. C. Roberge and J. A. Herman, *Can. J. Chem.*, 1964, **42,** 2262.
[4] J. Spence, *J. Amer. Chem. Soc.*, 1933, **55,** 1290.
[5] W. Bernstein and R. Schuler, *Nucleonics*, 1955, **13,** (11), 110.
[6] R. Schindler, *Radiochim. Acta*, 1963, **2,** 69.
[7] R. Schuler and R. Petry, *J. Amer. Chem. Soc.*, 1956, **78,** 5756.
[8] E. Hornig and J. Willard, *J. Amer. Chem. Soc.*, 1957, **79,** 2429.
[9] J. A. Herman and P. C. Roberge, *Trans. Faraday Soc.*, 1969, **65,** 1315.
[10] R. A. Gillis, R. R. Williams, Jr. and W. H. Hamill, *J. Amer. Chem. Soc.*, 1960, **82,** 5974; 1961, **83,** 17.
[11] P. C. Roberge and J. A. Herman, *Can. J. Chem.*, 1967, **45,** 1361.
[12] J. W. Schulte, *J. Amer. Chem. Soc.*, 1957, **79,** 4643.
[13] J. D. Spurny, *Int. J. Appl. Rad. Isotopes*, 1963, **14,** 337.
[14] P. M. Hupin, *Ph.D. Thesis*, (Laval University, 1963).
[15] A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, 1960, **82,** 519.
[16] R. Platzman, *Rad. Res.*, 1962, **17,** 419.
[17] M. A. West, *M.Sc. Thesis*, (Univ. of Saskatchewan, 1966).
[18] R. Leblanc, *Ph.D. Thesis*, (Laval University, 1968).
[19] D. T. Clark and J. M. Tedder, *Trans. Faraday Soc.*, 1966, **62,** 393.
[20] M. G. Bellas, J. K. S. Wan, W. F. Allen, O. P. Strausz and H. E. Gunning, *J. Phys. Chem.*, 1964, **68,** 2170.
[21] R. E. Fox and R. K. Curran, *J. Chem. Phys*, 1961, **34,** 1595.
[22] J. H. Sullivan and N. Davidson, *J. Chem. Phys*, 1951, **19,** 145.
[23] G. Martens, *Ph.D. Thesis*, (Université Libre de Bruxelles, 1960).
[24] J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Rad. Res.*, 1962, **17,** 379.
[25] E. L. Frankevich, *Russ. Chem. Rev.*, 1966, **35,** (7), 487, (Eng. trans.).
[26] J. R. Roberts and W. H. Hamill, *J. Phys. Chem.*, 1963, **67,** 2446.
[27] W. H. Seitzer and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1955, **77,** 2687.
[28] L. Bouby, A. Chapiro, M. Magat and N. Gislon, *Z. Elektrochem.*, 1958, **62,** 307.
[29] A. Chapiro, *J. Phys. Chem.*, 1959, **63,** 801.
[30] E. Collinson, F. S. Dainton and H. Gillis, *J. Phys. Chem.*, 1961, **65,** 695.

Published on 01 January 1969. Downloaded by Michigan State University on 19/01/2016 11:57:25.