IV and Fig. 3. The most probable reactions of acetyl in the presence of diacetyl are the decomposition and the association of two radicals to reform diacetyl. If these reactions of acetyl are both heterogeneous or both homogeneous, addition of nitrogen may be expected to have no effect on the carbon monoxide yield.[13] If one of the two reactions is homogeneous and the other heterogeneous, however, the rate of diffusion of acetyl to the wall and consequently the carbon monoxide yield should be affected by addition of nitrogen. The experiment listed in Table I shows no effect when approximately four times as much nitrogen as diacetyl is present, a result which has been confirmed by other experiments with various pressures of nitrogen. We therefore conclude that the reactions are either both homogeneous or both heterogeneous.

The variation of the carbon monoxide yield with diacetyl pressure illustrates the competition between the decomposition and association reactions of the acetyl radical. For the mechanism

$$\begin{aligned} A_2 + h\nu &= 2A \\ A &= CH_3 + CO \\ 2A &= A_2 \qquad (A = CH_3CO) \end{aligned}$$

it can be shown that for small fraction of light absorbed, constant incident light intensity, and small fraction of diacetyl decomposed, the carbon monoxide yield as we have defined it[14] is proportional to the quantity $[-C + \sqrt{C^2 + (A_2)}]/(A_2)$, where C is a constant. Although the fraction of the diacetyl decomposed at very low pressures was not small, the experimental curve in Fig. 3 is very similar in form to those obtained by plotting the above quantity as a function of diacetyl concentration. The deviations from the theoretical expression are best shown by a plot of the reciprocal of the carbon monoxide yield against diacetyl concentration; whereas the experimental points show almost linear variation with diacetyl concentration, those derived from the theoretical expression decrease in slope and deviate from linearity at high diacetyl pressures. This type of deviation might be expected if some diacetyl is reformed homogeneously by a 3-body process.

We are indebted to Mr. J. E. Tuttle for assistance with some of the experiments.

Summary

A study has been made of the carbon monoxide yield in the photolyses of acetone, diacetyl, and acetyl bromide between 0 and 140°. The results have been interpreted in terms of various reactions of the acetyl radical. It is concluded that the acetyl radicals are formed with such high energies that some of them decompose spontaneously into methyl and carbon monoxide. If this initial surplus of energy is lost by collisions, the radicals may either decompose or add to form diacetyl, the decomposition becoming increasingly important above 50°. The conditions under which these reactions occur and also the effect of adding nitric oxide have been discussed.

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[13] It is possible that nitrogen may act as a third body in the association of two acetyl radicals, but it is known that nitrogen is not generally an efficient third body.

[14] Carbon monoxide yield = $(d(CO)/dt)/(A_2)$.

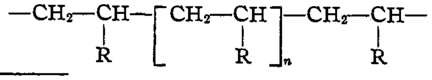
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Removal of Substituents from Vinyl Polymers. II[1]

BY FREDERICK T. WALL

When polyvinyl chloride or a copolymer of vinyl chloride and vinyl acetate is treated with zinc, part of the chlorine is removed as zinc chloride.[2] All of the chlorine is not removed because random removal of some of the atoms leaves others isolated in such a way that they can no longer be taken out. The amount of chlorine which remains after treatment with zinc depends upon the composition of the polymer and upon its structure.

The problem of calculating the fraction of chlorine remaining after treatment with zinc is a statistical one which has been considered for certain cases by P. J. Flory[3] and by F. T. Wall.[1] If the substituents are all in 1–3 relationship, such as



$$-CH_2-\underset{R}{\underset{|}{CH}}-\left[CH_2-\underset{R}{\underset{|}{CH}}\right]_n-CH_2-\underset{R}{\underset{|}{CH}}- \qquad (A)$$

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[1] For an earlier paper on this subject see THIS JOURNAL, **62**, 803 (1940).

[2] C. S. Marvel, J. H. Sample and Max F. Roy, *ibid.*, **61**, 3241 (1939).

[3] P. J. Flory, *ibid.*, **61**, 1518 (1939).

where R represents a substituent (either a chlorine or an acetate), then the fraction of the original chlorine which can be expected to remain is given by[1]

$$f = e^{-2x} \qquad (1)$$

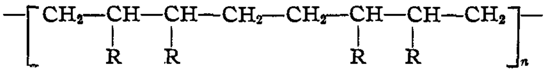
In this expression, x equals the chlorine mole fraction of the substituents. This equation was derived on the assumption that 1–3 pairs of chlorines could be removed by means of zinc and that 1–5 or more widely separated chlorines could not be removed at all.

On the other hand, if the vinyl units are oriented at random, so that 1–2, 1–3 and 1–4 relationships will exist, then the fraction is given by[1]

$$f = e^{-x}(1 - x/2) \qquad (2)$$

Here it was assumed that 1–2 and 1–3 pairs could be removed with equal ease and that more widely separated pairs could not be removed at all.

It seems desirable now to consider a third case, namely, that in which the mixed polymer has no substituents in 1–3 relationship, but which consists of alternate "head to head—tail to tail" hookups:



$$-\left[\mathrm{CH_2{-}\underset{R}{\underset{|}{CH}}{-}\underset{R}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}\underset{R}{\underset{|}{CH}}{-}\underset{R}{\underset{|}{CH}}{-}CH_2}\right]_n- \qquad \mathrm{(B)}$$

In this case the fraction f will be different from that in either of the first two cases. Since it has been established by Marvel and Cowan[4] that the pure methyl α-haloacrylates polymerize according to scheme (B), it is conceivable that some copolymers will have similar structures. Accordingly it appears worth while to investigate this possibility statistically.

Statistical Treatment.—For a given sample of polymer, let N_x equal the number of substituents which are halogens and N_y the number of substituents which are inert with respect to removal by zinc. The inert substituents can be regarded as dividing up the long polymer into groups of halides, such groups being isolated from each other. Assuming the substituents to be distributed throughout the long polymer at random, then the number of groups of vinyl halide units i members long will be given by

$$p_i = N_x(1 - x)^2x^{i-1} \qquad (3)$$

where

$$x = N_x/(N_x + N_y) \qquad (4)$$

Equation (3) was established in an earlier publication,[1] so it will be used here without further explanation.

If S_i'' is the number of halogen atoms that can be expected to remain (after treatment with zinc) in a group originally containing i vinyl halide units, then

$$f = \sum_i p_iS_i''/N_x = \sum_i S_i''(1 - x)^2x^{i-1} \qquad (5)$$

In order to complete the problem, we need only determine S_i'' and then perform the indicated summation in equation (5).

When the polymer (B) is treated with zinc, all pairs of halogens which are 1–2 to each other will be removed. If a halogen has as its nearest neighbor an inert substituent, that halogen is isolated and hence incapable of being removed. It is obvious that when i is odd, there will be exactly one isolated halogen atom in the group, because all but one halogen will be paired. When i is even, half of the groups will have two isolated halogens (one at each end) and the other half will have no isolated halogens. Thus, even when i is not odd, there will be on the average one halogen left per group for a sufficiently large number of groups. Accordingly $S_i'' = 1$ for all values of i greater than zero.

Substituting $S_i'' = 1$ into the equation (5) we find that

$$\begin{aligned} f &= \sum_i (1 - x)^2x^{i-1} \\ &= (1 - x)^2(1 + x + x^2 + x^3 + \ldots) \qquad (6) \\ &= 1 - x \end{aligned}$$

Discussion.—The simple result expressed by equation (6) is readily seen to have the proper limiting characteristics. If $x = 1$, the polymer contains no inert substituents and hence no halogens are isolated with the result that $f = 0$. As $x \longrightarrow 0$, all of the halogens become isolated so that $f \longrightarrow 1$.

Values of f as a function of x are plotted for the three cases in Fig. 1. The differences between those cases are sufficient to enable one to get a fair idea as to the nature of the polymer by comparing experimentally observed fractions with the different theoretical amounts.

It should be emphasized that the results expressed by equations (1), (2) and (6) are valid only if the reaction probabilites of the individual vinyl molecules—such as vinyl chloride and vinyl acetate—are equal during the formation of the polymer. In that case the group distribution will be entirely random as assumed, and equation (3)

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(4) C. S. Marvel and J. C. Cowan, This Journal **61**, 3156 (1939).

will be true. If during the formation of the polymer, one of the compounds tends to react faster than the other, the first portion of polymer formed will have a different composition from that formed later. The resulting polymer will not have the same properties as that arising from a mixture of molecules having equal reaction velocities even though the final average compositions are the same. The effect of different reaction rates of formation is now under consideration, the results so far being in agreement with the findings of Staudinger and Schneiders,[5] who observed that mixed vinyl chloride–vinyl acetate polymers could be fractionated into portions of different compositions. The theoretical treatment will be published shortly.

Effect of Different Rates of Removal of Substituents.—Let us now turn to a consideration of the assumptions involved in the derivation of equation (2). It was assumed that 1–2 and 1–3 pairs of substituents could be removed with equal ease and that 1–4 or more widely separated substituents could not be removed at all. Actually it is not necessary to suppose that the specific rates of removal of 1–2 and 1–3 pairs are equal. Flory[3] showed in connection with a randomly oriented polyvinyl halide that the same result would be obtained if 1–2 removals took place infinitely more easily than 1–3 removals or *vice versa*. Since these three extreme cases all gave the same answer, Flory suggested that a similar result would be obtained for any relative rate of removal of 1–2 and 1–3 pairs. It will now be proved rigorously that Flory's surmise is correct.

Consider a polyvinyl halide made up of randomly oriented vinyl units. Let us denote a vinyl unit with its substituent on the right-hand carbon (—CH$_2$—CHR—) by means of a + sign and a vinyl unit with its substituent on the left-hand carbon (—CHR—CH$_2$—) by means of a − sign. Then a portion of the polymer might look as follows

$$+-|+++-----|+--|+-|++--- \qquad \text{(C)}$$

Each time a plus sign is followed by a minus sign, one has a 1–2 pair of substituents; and each time a minus sign is followed by a plus sign, one has a 1–4 pair. Whenever a plus or minus sign is followed by another like itself, there is represented a 1–3 pair of substituents. Assuming that 1–4 pairs cannot be removed by means of zinc, the polymer is seen to be broken up into isolated groups, bounded by the vertical lines in the array (C). Each isolated group begins with a plus sign and ends with a minus sign, there being $n-1$ possible groups consisting of n members.

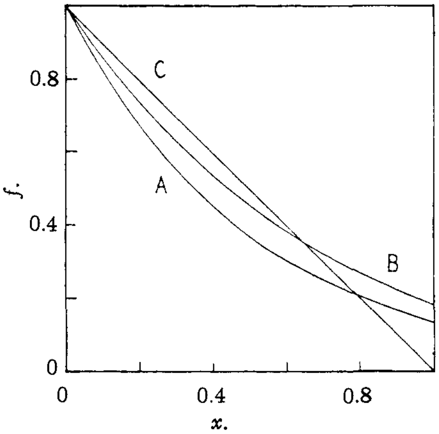

Fig. 1.—Fraction of halogen remaining in mixed vinyl polymer after treatment with zinc; x = halogen mole fraction of substituents: A, "head to tail" polymer, $f = e^{-2x}$; B, random polymer, $f = e^{-x}(1 - x/2)$; C, "head to head–tail to tail" polymer, $f = 1 - x$.

Suppose a group of n members has $n-j$ plus signs and j minus signs. Let $S_{n-j,j}$ equal the halogen expectancy for such a group after treatment with zinc. Obviously $S_{j,n-j} = S_{n-j,j}$. Also, let S_n equal the halogen expectancy of a group consisting of n vinyl units all oriented in the same direction. Now if the group $n-j$, j is attacked by zinc, the first pair of halogens can be removed in any of $n-1$ ways. There will be $n-2$ ways of taking out a 1–3 pair and one way of removing a 1–2 pair. Let k_1 and k_2 represent specific reaction rates for the removal of 1–3 and 1–2 pairs, respectively. Then if $1 < j < n-1$, we note by considering all possible removals that

$$\begin{aligned}[(n-2)k_1 + k_2]S_{n-j,j} = {} & k_1(S_0 + S_1 + \ldots S_{n-j-3} + S_{n-j-2}) \\ & + k_1(S_{n-j-2,j} + S_{n-j-3,j} + \ldots S_{1,j} + S_{0,j}) \\ & + k_2(S_{n-j-1} + S_{j-1}) \qquad (7) \\ & + k_1(S_{n-j,0} + S_{n-j,1} + \ldots S_{n-j,j-3} + S_{n-j,j-2}) \\ & + k_1(S_{j-2} + S_{j-3} + \ldots S_1 + S_0)\end{aligned}$$

or

$$\begin{aligned}[(n-2)k_1 + k_2]S_{n-j,j} = {} & k_1 \sum_{i=0}^{n-j-2} (S_i + S_{i,j}) \\ & + k_2(S_{n-j-1} + S_{j-1}) \qquad (8) \\ & + k_1 \sum_{i=0}^{j-2} (S_{n-j,i} + S_i)\end{aligned}$$

If $j = 1$, the third term is omitted from equation (8) and if $j = n - 1$, the first term is omitted.

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[5] H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

Making use of the following relationship developed by Flory[3]

$$S_m = \frac{2}{m-1}\sum_{i=0}^{m-2} S_i \qquad (9)$$

equation (8) becomes

$$[(n-2)k_1 + k_2]S_{n-j,j} = \frac{k_1(n-j-1)}{2}S_{n-j} + k_1\sum_{i=0}^{n-j-2} S_{i,j} + k_2(S_{n-j-1} + S_{j-1}) + k_1\sum_{i=0}^{j-2} S_{n-j,i} + \frac{k_1(j-1)}{2}S_j \qquad (10)$$

Now let P_n equal the average halogen expectancy for the $n-1$ equally probable possibilities of groups consisting of n members. Then

$$P_n = \frac{S_{n-1,1} + S_{n-2,2} + \ldots S_{2,n-2} + S_{1,n-1}}{n-1} \qquad (11)$$

or

$$(n-1)P_n = \sum_{j=1}^{n-1} S_{n-j,j} \qquad (12)$$

It follows from equations (10) and (12) that

$$[(n-2)k_1 + k_2](n-1)P_n = \frac{k_1}{2}\sum_{j=1}^{n-2}(n-j-1)S_{n-j} + k_1\sum_{j=1}^{n-2}\sum_{i=0}^{n-j-2} S_{i,j} + k_2\sum_{j=1}^{n-1} S_{n-j-1} + S_{j-1}) + k_1\sum_{j=2}^{n-1}\sum_{i=0}^{j-2} S_{n-j,i} + \frac{k_1}{2}\sum_{j=2}^{n-1}(j-1)S_n \qquad (13)$$

$$= k_1\sum_{j=2}^{n-1}(j-1)S_j + k_2(n-1)S_n + 2k_1\sum_{j=2}^{n-2}\sum_{i=1}^{n-j-1} S_{i,n-i-j} + 2k_1\sum_{j=1}^{n-2} S_{0,j} \qquad (14)$$

$$= k_1\sum_{j=2}^{n-1}(j-1)S_j + k_2(n-1)S_n + k_1(n-1)S_n + 2k_1\sum_{j=2}^{n-2}(n-j-1)P_{n-j} \qquad (15)$$

$$= k_1\sum_{j=2}^{n}(j-1)S_j + k_2(n-1)S_n + 2k_1\sum_{j=2}^{n-2}(j-1)P_j \qquad (16)$$

or

$$P_n = \frac{k_1\left[\sum_{j=2}^{n}(j-1)S_j + 2\sum_{j=2}^{n-2}(j-1)P_j\right] + k_2(n-1)S_n}{(n-2)\,(n-1)k_1 + (n-1)k_2} \qquad (17)$$

It is seen from equation (17) that in order to prove $P_n = S_n$, one needs only show that

$$\sum_{=2}^{n}(j-1)S_j + 2\sum_{j=2}^{n-2}(j-1)P_j = (n-2)(n-1)S_n \qquad (18)$$

This proof can be carried out by means of induction. First let us prove that

$$\sum_{j=2}^{n}(j-1)S_j + 2\sum_{j=2}^{n-2}(j-1)S_j = (n-2)(n-1)S_n \qquad (19)$$

By direct substitution, expression (19) can be verified for values of n such as 4 and 5. Then if (19) is true for some value of n (such as 4 or 5) it follows that

$$\sum_{j=2}^{n+1}(j-1)S_j + 2\sum_{j=2}^{n-1}(j-1)S_j = (n-2)(n-1)S_n + nS_{n+1} + 2(n-2)S_{n-1} \qquad (20)$$

Using equation (9) for rearranging the right-hand side of expression (20), we see that

$$\sum_{j=2}^{n+1}(j-1)S_j + 2\sum_{j=2}^{n-1}(j-1)S_j = n(n-1)S_{n+1} \qquad (21)$$

But expression (21) bears the same relationship to $n+1$ as expression (19) does to n. Hence if expression (19) is true for some value of n (as we know it to be) it must be true for $n+1$, etc. Therefore, equation (19) must be true for all positive integral values of n.

Now it is obvious that $P_2 = S_2$. Hence equation (18) must be true for $n = 4$ by reason of relationship (19) which was just proved. Therefore $P_4 = S_4$ because of equation (17). It is also obvious that $P_3 = S_3$. Hence by equations (19), (18) and (17), $P_5 = S_5$. This process can now be continued indefinitely, thus completing the proof that

$$P_n = S_n \qquad (22)$$

It follows from equation (22) that the *average* halogen expectancy for groups consisting of n vinyl units with no 1–4 linkages is independent of the relative rates of removal of 1–2 or 1–3 pairs of substituents. We can accordingly remove the assumption involved in the derivation of equation (2) that 1–2 and 1–3 removals take place with equal ease.

Summary

The removal of substituents from mixed vinyl polymers by means of zinc is treated statistically for the case when the polymer is made up of "head to head—tail to tail" units. The results are compared with previously derived formulas for other structures. It is proved rigorously that different removal rates of 1–2 and 1–3 halogen pairs has no effect on the final percentage of halogen remaining in a randomly oriented polymer.

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