cules is developed and it is shown that the sum of the dipole moments of two states resulting from resonance is the same as the sum of the dipole moments of the original states. Assuming a wave function $\psi = \psi_c + a\psi_i$ for a system resonat-ing between covalent and ionic states, upper and lower limits to $|a|$ are calculated using dipole moment data, and the results compared to calculations of $|a|$ based on energy values.

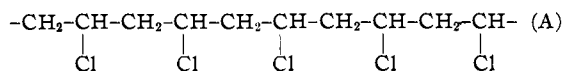URBANA, ILLINOIS          RECEIVED JANUARY 15, 1940

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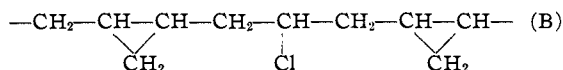# Removal of Substituents from Vinyl Polymers

## BY FREDERICK T. WALL

Experimental studies by Marvel and co-workers[1] have shown that chlorine can be partly removed from vinyl chloride polymers by means of zinc. The removal of chlorine is not quantitative, however, owing to the fact that some of the chlorides become isolated. A given chlorine atom is considered isolated when its nearest neighbor is so far away that it and that neighbor can no longer be removed as a pair by means of zinc.

This notion can be illustrated as follows. Suppose the polymer has all its substituents in 1–3 relationship with respect to their nearest neighbors. Then a portion of the polymer would look as follows

$$-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH- \quad (A)$$
$$\quad\quad | \quad\quad\quad | \quad\quad\quad | \quad\quad\quad | \quad\quad\quad |$$
$$\quad\quad Cl \quad\quad Cl \quad\quad Cl \quad\quad Cl \quad\quad Cl$$

If this portion of the polymer were attacked by zinc, some of the chlorides might be removed in any of several ways. If, say, zinc removed the first and last pairs, there would result

$$-CH_2-CH-CH-CH_2-CH-CH_2-CH-CH- \quad (B)$$
$$\qquad\quad \diagdown\diagup \qquad\quad | \qquad\quad \diagdown\diagup$$
$$\qquad\quad CH_2 \qquad\quad Cl \qquad\quad CH_2$$

in which the middle chloride is now isolated and hence incapable of removal.

Assuming that zinc removes chlorides in a perfectly random way, the problem of what fraction of the chlorides becomes isolated is simply a question of probability. This problem has been solved by Flory[2] for the cases where all of the substituents are the same. His results show that if the polymer has all of its chlorides in 1–3 relationship, then the portion $1/e^2$ (or 13.53%) of the original chlorides will become isolated, a result for which there is experimental support.[1] This was derived after making the

reasonable assumption that no two chlorides separated by more than three carbons can be removed as a pair.

Flory also considered the case where the polymer is not necessarily 1–3 throughout, but is made up of vinyl units oriented at random. Since a given vinyl unit can be oriented in either of two ways along the line of the polymer chain, 1–2, 1–3 and 1–4 relationships will exist between substituents. Assuming that 1–2 and 1–3 substituents can be removed with equal ease but that 1–4 or more widely separated substituents cannot be removed, he showed that the portion $1/2e$ (or 18.40%) of the original substituents could be expected to remain after reaction.

More recently, Marvel and Mastin[3] have studied the removal of chlorine from mixed vinyl chloride vinyl acetate polymers. In such a case, the acetates will divide up the long polymer into isolated groups of chlorides. Assuming that the acetates are interspersed at random in the polymer, one is confronted with a more general statistical problem in attempting to calculate the fraction of the original chlorides which can be expected to remain after treatment with zinc. In this paper, the solution to that problem is given for the two cases when the linkages are all 1–3 and when the orientations are random.

Statistical Treatment.—In attacking both cases of this problem, it is first to be noted that any two chlorides which have one or more acetates between them as substituents along the chain cannot be removed as pairs by means of zinc. The problem then resolves itself first into finding the number of groups of chlorides of given lengths formed by interspersing acetates, and, second, into summing up those numbers multiplied by the chloride expectancy per group. The chloride expectancy per group depends upon whether or

(1) C. S. Marvel, J. H. Sample and Max F. Roy, THIS JOURNAL, 61, 3241 (1939).

(2) P. J. Flory, ibid., 61, 1518 (1939).

(3) Private communication.

not the linkages are all 1–3 or are random. The number of groups of specified lengths, however, does not depend upon the presence or absence of link orientation restrictions, as far as probability alone is concerned.

We shall accordingly first turn to the problem of group distribution. Let $N_X$ equal the total number of X's (chlorides) and $N_Y$ the total number of Y's (acetates) in the long polymer. In the following treatment it will be assumed that these $N$'s are very large numbers. Then if $p_i$ equals the number of groups of X's containing $i$ members, it follows that

$$N_X = \sum_i i p_i \qquad (1)$$

and

$$N_Y = \sum_i p_i \qquad (2)$$

In order for (2) to be valid, it is necessary that we include values for $i = 0$. Regarding the Y's as spacers, two adjacent Y's surround a group of X's zero members long. Each group of X's has one Y as a spacer; hence the equality (2).

Now the number of complexions in the statistical state represented by $p_0$, $p_1$, $p_2$, . . . is given by

$$W = \frac{N_Y!}{p_0! p_1! p_2! \ldots} \qquad (3)$$

The most probable distribution corresponds to the maximum value for $W$. Using Stirling's approximation for $\ln W$ and setting the variation of it equal to zero, we have[4]

$$\delta \ln W = - \sum_i \ln p_i \, \delta p_i = 0 \qquad (4)$$

This equation is subject to two additional equations obtained by taking variations of (1) and (2).

$$\delta N_X = \sum_i i \, \delta p_i = 0 \qquad (5)$$

$$\delta N_Y = \sum_i \delta p_i = 0 \qquad (6)$$

Introducing Lagrangian multipliers and combining in the usual way, we find that

$$p_i = e^{-\lambda - \mu i} \qquad (7)$$

To determine $\mu$ and $\lambda$, equation (7) is combined with equation (1) and with equation (2), giving

$$N_X = \sum_i i e^{-\lambda - \mu i} = e^{-\lambda - \mu} \{1 + 2e^{-\mu} + 3e^{-2\mu} + \ldots\}$$
$$= \frac{e^{-\lambda} e^{-\mu}}{(1 - e^{-\mu})^2} \qquad (8)$$

(4) This treatment is similar to that employed in deriving the Maxwell–Boltzmann distribution law; see for example, Tolman, "Statistical Mechanics," Oxford University Press, 1938.

and

$$N_Y = \sum_i e^{-\lambda - \mu i} = e^{-\lambda} \{1 + e^{-\mu} + e^{-2\mu} + \ldots\}$$
$$= \frac{e^{-\lambda}}{1 - e^{-\mu}} \qquad (9)$$

From (8) and (9) it is found that

$$e^{-\mu} = \frac{N_X}{N_X + N_Y} \qquad (10)$$

and

$$e^{-\lambda} = \frac{N_Y^2}{N_X + N_Y} \qquad (11)$$

Substituting (10) and (11) into (7), we find

$$p_i = \frac{N_Y^2}{N_X + N_Y} \left( \frac{N_X}{N_X + N_Y} \right)^i \qquad (12)$$

Define

$$x = \frac{N_X}{N_X + N_Y} \qquad (13)$$

Then

$$p_i = N_X (1 - x)^2 x^{i-1} \qquad (14)$$

Equation (14) tells us the number of groups of X's containing $i$ members in terms of the mole fraction of substituents which are of the X variety and the total number $N_X$.

If the average number of X's (chlorides) remaining after treatment with zinc is $S_i$ for a group originally containing $i$ members, then the total number $N_r$ of X's remaining in the infinite polymer is

$$N_r = \sum_i S_i p_i \qquad (15)$$

and the fraction, $f$, of the original number is

$$f = \frac{N_r}{N_X} = \sum_i S_i (1 - x)^2 x^{i-1} \qquad (16)$$

Expanding and rearranging

$$f = \sum_i S_i (x^{i-1} - 2x^i + x^{i+1})$$
$$= \sum_i (S_{i+1} - 2S_i + S_{i-1}) x^i \qquad (17)$$

Defining $\Delta_n = S_n - S_{n-1}$ we see that

$$f = \sum_i (\Delta_{i+1} - \Delta_i) x^i \qquad (18)$$

**Case 1: 1–3 Coupling Throughout.**—If all of the substituents are 1–3 with respect to each other, then $\Delta_{i+1} - \Delta_i$ is subject to a relationship derived by Flory,[2] namely

$$\Delta_{i+1} - \Delta_i = (-2)^i / i! \qquad (19)$$
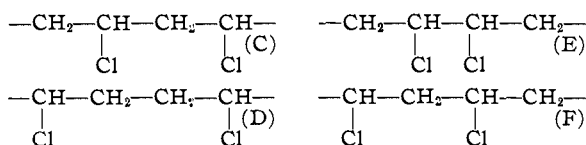
Substituting into (18)

$$f = \sum_i \frac{(-2)^i}{i!} x^i = e^{-2x} \qquad (20)$$

Equation (20) gives a very simple expression for the fraction of chlorine remaining after

treatment with zinc. If $x = 1$, which would be the case when all of the substituents are chlorides, $f = 1/e^2$ in agreement with Flory's result for that special case. On the other hand, it is seen that the smaller the value of $x$, the greater will be the fraction of original chlorides remaining at the end. This follows because of the tendency of acetates to isolate many chlorides. Preliminary experimental evidence obtained by Marvel and Mastin[5] supports the validity of the result $f = e^{-2x}$.

**Case 2: Random Coupling Throughout.—** In the event that the vinyl links join together in a random way, the chloride expectancy per group will not be the same as for the case where all the linkages are 1–3, assuming that 1–4 or more widely separated pairs cannot be removed by zinc. Consider, for example, the situation possible for a group containing two vinyl units. Four possibilities will exist, namely

$$\begin{array}{ll}
-CH_2-CH-CH_2-CH- & -CH_2-CH-CH-CH_2- \\
\qquad\quad | \qquad\quad\;\; |\;\;(C) & \qquad\quad | \quad\; |\;\;(E) \\
\qquad\quad Cl \qquad\quad Cl & \qquad\quad Cl \;\; Cl \\
\\
-CH-CH_2-CH_2-CH- & -CH-CH_2-CH-CH_2- \\
\;\;| \qquad\qquad\qquad\;\; |\;(D) & \;\;| \qquad\quad\; |\;(F) \\
\;\;Cl \qquad\qquad\qquad Cl & \;\;Cl \qquad\quad Cl
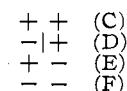\end{array}$$

Of the four possibilities, C, E and F will have no chlorides remaining after treatment with zinc, whereas D will have two remaining. If each possibility is equally probable, then the average number of chlorides remaining from randomly built up groups of two vinyl units will be 2/4 or 1/2 per group. This value, which we will denote by $S_2'$, is different from the $S_2$ value for 1–3 orientation, which equals zero.

The problem in case 2 is precisely the same as that of case 1 up through equation (18). That is

$$f' = \sum_i (\Delta'_{i+1} - \Delta'_i)x^i \qquad (18')$$

the primes serving to distinguish case 2 from case 1.

Consider once more the situation for $n = 2$. By the use of $+$ and $-$ signs, where a plus sign denotes a vinyl unit with its substituent on the right-hand side and a minus sign denotes a vinyl unit with its substituent on the left-hand side, the array CDEF can be abbreviated as follows.

$$\begin{array}{ll}
+\;+ & (C) \\
-\,|+ & (D) \\
+\;- & (E) \\
-\;- & (F)
\end{array}$$

(5) Private communication. Their results will be published soon.

For $n$ greater than 2, similar arrays of $2^n$ members could be set up. Whenever a minus sign is followed by a plus sign, the member is divided into two smaller groups (indicated by the vertical line in D above). For $n = 3$ we would have the array

$$\begin{array}{llll}
+\;+\;+ & & +\;+\;- & \\
-\,|+\;+ & & -\,|+\;- & \\
+\;-\,|+ & & +\;-\;- & (G) \\
-\;-\,|+ & & -\;-\;- &
\end{array}$$
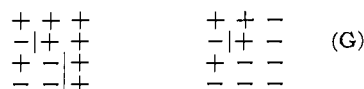
where four of the members are broken up by minus signs followed by plus signs. Direct counting would then tell us that $S_3' = 1$.

Let us now consider the case of a general array each of whose $2^n$ members will be considered equally probable. For a particular value of $n$, let $r_i$ equal the number of groups $i$ members long ending with $+$ signs on the right and let $s_i$ equal the number of groups $i$ members long ending with $-$ signs in the extreme right-hand column. Also let $l_i$ equal the number of groups (ending with $-$ signs) without their terminal symbol in the extreme right-hand column. It follows then, that

$$2^n S_n' = (r_1 + s_1 + l_1)S_1 + (r_2 + s_2 + l_2)S_2 + \\
\dots + (r_n + s_n + l_n)S_n \qquad (21)$$

assuming 1–2 and 1–3 removals are equally probable.

Now in going from the array of $2^n$ members to the next higher array, one need only add $+$ signs to all members of the $n$ array and then $-$ signs to all members of the $n$ array to arrive at the $2^{n+1}$ members of the $n + 1$ array. The effect of adding $+$ or $-$ signs upon the classes of groups defined in the previous paragraph is apparent. We see that

$$2^{n+1}S_{n+1}' = (2^{n-1} + s_1 + 2l_1)S_1 + (2r_1 + \\
s_1 + s_2 + 2l_2)S_2 + (2r_2 + s_2 + s_3 + 2l_3)S_3 + \\
\dots + (2r_n + s_n)S_{n+1} \qquad (22)$$

where the $r_i$'s, $s_i$'s and $l_i$'s refer back to the case of $n$ members. Combining (21) and (22)

$$2^{n+1}(S_{n+1}' - S_n') = (2^{n-1} - 2r_1 - s_1)S_1 + \\
(2r_1 + s_1 - 2r_2 - s_2)S_2 + (2r_2 + s_2 - 2r_3 - \\
s_3)S_3 + \dots + (2r_n + s_n)S_{n+1} \qquad (23)$$

Rearranging (23)

$$2^{n+1}\Delta_{n+1}' = 2^{n-1}S_1 + (2r_1 + s_1)\Delta_2 + (2r_2 + s_2)\Delta_3 + \\
\dots + (2r_{n-1} + s_{n-1})\Delta_n + (2r_n + s_n)\Delta_{n+1} \qquad (24)$$

But by an inductive method for the various arrays, it can be shown that

$$r_j = 2^{n-j-1} \text{ and } s_j = 2^{n-j-1}(j - 1) \text{ for } j < n \qquad (25) \\
\text{and } r_j = 1 \quad \text{and } s_j = n \quad \text{for } j = n$$

Combining the results expressed by (25) with equation (24) there is obtained

$$\Delta'_{n+1} = \frac{S_1}{2^2} + \frac{2\Delta_2}{2^3} + \frac{3\Delta_3}{2^4} + \cdots + \frac{n\Delta_n}{2^{n+1}} + \frac{(n+2)\Delta_{n+1}}{2^{n+1}} \quad (26)$$

Also

$$\Delta'_n = \frac{S_1}{2^2} + \frac{2\Delta_2}{2^3} + \frac{3\Delta_3}{2^4} + \cdots + \frac{(n+1)\Delta_n}{2^n} \quad (27)$$

Subtracting (27) from (26) we see that

$$\Delta'_{n+1} - \Delta'_n = \frac{n+2}{2^{n+1}}(\Delta_{n+1} - \Delta_n) \quad (28)$$

But

$$\Delta_{n+1} - \Delta_n = \frac{(-2)^n}{n!} \quad (19)$$

Hence

$$\Delta'_{n+1} - \Delta'_n = \frac{(2+n)(-1)^n}{2n!} \quad (29)$$

Substituting (29) into (18') there results

$$f' = \sum_i \frac{(2+i)(-1)^i}{2i!}x^i$$

$$= \sum_i \frac{(-x)^i}{i!} - \frac{x}{2}\sum_i \frac{(-x)^{i-1}}{(i-1)!}$$

$$= e^{-x} - \frac{x}{2}e^{-x} = e^{-x}\left(1 - \frac{x}{2}\right) \quad (30)$$

The result expressed by equation (30) is also a simple result, yet substantially different from that applying to case 1, namely, $f = e^{-2x}$. It should be noted that if $x = 1$, equation (30) gives $f' = 1/2e$ in agreement with Flory's result for that special case.

### Discussion

A certain amount of evidence as to the nature of the vinyl polymers can be obtained by seeing which of the two formulas $e^{-2x}$ or $e^{-x}(1 - x/2)$

best predicts the fraction of chlorine isolated in the mixed polymers. Preliminary evidence obtained by Marvel and Mastin[5] indicates that the former expression is the better of the two. This alone would not prove the 1-3 hypothesis, since the same result could be obtained with the random distribution, if 1-2, 1-3 and 1-4 pairs could be drawn off with equal ease and 1-5 or higher pairs not removed at all. However, agreement with the formula $e^{-2x}$ would substantiate other evidence[1] for the 1-3 hypothesis.

The author is indebted to Professor Marvel and Mr. Mastin for bringing this problem to his attention.

### Summary

By statistical methods, formulas are developed to predict the fraction of chlorine remaining in mixed vinyl chloride–vinyl acetate polymers upon treatment with zinc, assuming the acetates to be distributed in a random manner. Two cases are considered: first, 1-3 coupling throughout with the assumption that only 1-3 pairs of chlorides can be removed; second, random coupling with only 1-2 and 1-3 pairs of chlorides capable of removal by zinc, it being assumed that 1-2 and 1-3 removals are equally probable. These two cases yield the results $f = e^{-2x}$ and $f' = e^{-x} \cdot (1 - x/2)$ for the two respective cases where $x$ is the chlorine mole fraction of the substituents.

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## The Vapor Pressures of Certain Unsaturated Hydrocarbons

BY ARTHUR B. LAMB AND EDWIN E. ROPER

In connection with a study of the adsorption of the vapors of certain unsaturated hydrocarbons upon charcoal and other adsorbents, more accurate and extensive information as to the vapor pressures of these hydrocarbons was required than was available in the literature. The measurements of vapor pressure here presented were therefore made over a considerable range of temperature and, since our samples of hydrocarbons were of exceptional purity, with particular care.

Materials.—The hydrocarbons studied by us (Tables II–IV) were those used by Professor Kistiakowsky and his collaborators in their

studies of the heats of hydrogenation, etc., and were prepared in part by them and in part by them and ourselves jointly. We wish to express our appreciation of this generous arrangement. A description of the methods of preparation has already been published.[1]

The high purity of these hydrocarbons has been demonstrated by the close concordance of the heats of hydrogenation, boiling points, freezing points and other physical properties of different distillation fractions of the same samples

(1) (a) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935); (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935); (c) **58**, 137 and (d) 146 (1936).