Acknowledgment is made to the following members of the Petroleum Refining Laboratory for help in connection with the data compiled in Table IV: J. P. Haimovicz, G. Herbolsheimer, J. H. Jones, R. H. McCormick, A. E. Schubert, and K. A. Steel.

Summary

1. The identification of olefins as reported by Goldwasser and Taylor in their dehydration of certain alcohols is questioned.

2. The Podbielniak–Simons–Taylor column has an efficiency of about fifteen theoretical plates.

3. Fruitless efforts were made to separate by distillation through the Podbielniak–Simons–Taylor column two binary mixtures having boiling point spreads of 2.7 and 1.5°, and a ternary mixture having an over-all boiling point spread of 2.7°. Our failure is in sharp contrast to the reported separation and identification of six hexenes with an over-all boiling point spread of 2.5°.

4. The Podbielniak–Simons–Taylor column is compared in Table IV with other types of fractional distillation columns.

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

Ionic Character and Dipole Moments

BY FREDERICK T. WALL

In discussing the nature of the chemical bond in hydrogen halides, Pauling[1] has found it convenient to regard the normal states of those molecules as superpositions of ionic and covalent states. As a measure of the fraction of ionic character in the molecules he took the values of μ/er where μ is the dipole moment and r the internuclear separation. In this paper the notion is extended somewhat, and a theory of dipole moments for the normal and first excited states is developed.

In a previous paper[2] the author considered the problem by supposing that the wave function (unnormalized) for the molecule can be taken as

$$\psi = \psi_c + a\psi_i$$

where ψ_c is a purely covalent function and ψ_i a purely ionic function, and a is a parameter. To get the best energy value from that function, the energy expression was minimized with respect to a. If W represents that minimized value and W_c and W_i the covalent and ionic energies, then it was shown that

$$a^2 = \frac{W - W_c}{W - W_i} \qquad (1)$$

By use of equation (1) estimates of values for a^2 were obtained for the different hydrogen halides at their equilibrium internuclear separations and the results roughly correlated with dipole moment values.

A more precise relationship between dipole moment and ionic character will now be developed and some conclusions drawn from it. Using the function $\psi = \psi_c + a\psi_i$ in which ψ_c and ψ_i are each normalized to unity, then the general expression for the dipole moment becomes

$$\mu = \frac{\mu_{cc} + 2a\mu_{ci} + a^2\mu_{ii}}{1 + 2a\Delta + a^2} \qquad (2)$$

where μ_{cc} is the moment of the covalent structure, μ_{ii} that of the ionic structure and μ_{ci} the corresponding integral of the moment expression over the states ψ_i and ψ_c. That is

$$\mu_{ci} = \int \psi_c^*\mu\psi_i d\tau = \int \psi_i^*\mu\psi_c d\tau$$

Also

$$\Delta = \int \psi_c^*\psi_i d\tau = \int \psi_i^*\psi_c d\tau$$

Now the moment of the covalent structure can be taken as zero and that of the ionic structure as er. It remains then to find the value of μ_{ci}.

In order to get an idea as to the nature of μ_{ic}, consider the hypothetical case of resonance between HH and H^+H^-. (For the actual hydrogen molecule, the structure H^-H^+ is equally as important as H^+H^-,[3] but it will not be considered here in order that the results can be used for the hydrogen halides for which only the structures HX and H^+X^- are important.) Setting up a purely covalent function of the Heitler–London[4] type for HH and a simple ionic function such as was used by Weinbaum[3] for H^+H^-, the integral μ_{ic} readily can be evaluated. In this case it turns out that

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[1] Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, II-8.

[2] F. T. Wall, THIS JOURNAL, 61, 1051 (1939).

[3] S. Weinbaum, *J. Chem. Phys.*, 1, 593 (1933).

[4] W. Heitler and F. London, *Z. Physik*, 44, 455 (1927).

$$\mu_{ic} = \frac{\mu_{cc} + \mu_{ii}}{2}\,\Delta \tag{3}$$

where $\mu_{cc} = 0$ and $\mu_{ii} = er$.

The result expressed by equation (3) is a simple one which seems quite plausible. It will be assumed that (3) also holds for the hydrogen halides. Combining (3) with (2) there is obtained

$$\mu = \frac{\mu_{cc}(1 + a\,\Delta) + \mu_{ii}(a\,\Delta + a^2)}{1 + 2a\,\Delta + a^2} \tag{4}$$

Letting $\mu_{cc} = 0$ and $\mu_{ii} = er$, equation (4) becomes

$$\mu = \frac{a\,\Delta + a^2}{1 + 2a\,\Delta + a^2}\,er \tag{5}$$

Equations (4) and (5) can be demonstrated to be satisfactory in several ways. Obviously they have the correct characteristics for the two limiting cases when $a \longrightarrow 0$ (covalent) and when $a \longrightarrow \pm\infty$ (ionic). They are also highly satisfactory for the intermediate cases when $a = \pm 1$. If $a = \pm 1$, then

$$\mu = \frac{\mu_{cc} + \mu_{ii}}{2} \text{ from (4)}$$

or

$$\mu = {}^1/_2 er \text{ from (5)}$$

In other words, when the ionic and covalent states contribute equally, the moment is just the mean of the moments (or half the ionic moment).

It is also seen from (5) that whenever $-1 < a < 1$, then $0 < \mu < 1/2(er)$. This situation can be realized for the normal state of a molecule whenever the covalent state is more stable than the ionic state. The fact that hydrogen chloride, hydrogen bromide and hydrogen iodide all have dipole moments less than $1/2(er)$ is in agreement with this result and their assumed energy curves.

On the other hand, when $1 < a < \infty$ or $-1 > a > \infty$ then $\mu > 1/2(er)$. This state of affairs should exist for normal hydrogen fluoride according to Pauling's energy curves, because the ionic curve cuts below the covalent one. We should expect then that the dipole moment of hydrogen fluoride would be greater than $1/2(er)$.

Another interesting result can be derived as follows. The energy W for a system with a wave function $\psi_c + a\psi_i$ is given by

$$W = \frac{H_{cc} + 2aH_{ic} + a^2H_{ii}}{1 + 2a\,\Delta + a^2} \tag{6}$$

Letting $\partial W/\partial a$ equal zero and combining that result with equation (6), there is obtained a quadratic equation in a, the two roots of which are subject to the relations

$$\begin{aligned} a_1a_2 &= \frac{\Delta H_{cc} - H_{ic}}{H_{ic} - \Delta H_{ii}} \\ a_1 + a_2 &= \frac{H_{ii} - H_{cc}}{H_{ic} - \Delta H_{ii}} \end{aligned} \tag{7}$$

One of the roots (say a_1) corresponds to dissociation into neutral atoms and the other (a_2) to dissociation into ions. Each of the two resultant states has a dipole moment given by (4) or (5) by putting into those equations a_1 and a_2. But from (7) it can be shown that

$$1 + (a_1 + a_2)\,\Delta + a_1a_2 = 0 \tag{8}$$

which is precisely the condition for orthogonality of $\psi_c + a_1\psi_i$ and $\psi_c + a_2\psi_i$. But

$$\mu_1 + \mu_2 = \frac{\mu_{cc}(1 + a_1\,\Delta) + \mu_{ii}(a_1\,\Delta + a_1^2)}{1 + 2a_1\,\Delta + a_1^2} + \frac{\mu_{cc}(1 + a_2\Delta) + \mu_{ii}(a_2\,\Delta + a_2^2)}{1 + 2a_2\,\Delta + a_2^2} \tag{9}$$

Simplifying this expression and making use of (8), we find that

$$\mu_1 + \mu_2 = \mu_{cc} + \mu_{ii} \tag{10}$$

or if $\mu_{cc} = 0$ and $\mu_{ii} = er$

$$\mu_1 + \mu_2 = er \tag{11}$$

Equations (10) and (11) express the simple result that the total dipole moment of the two resultant states is equal to the sum of the moments of the interacting states. For that reason, the quantity μ/er is an excellent measure of ionic character even though it is not simply related to the quantity a.

The qualitative features of the relationship between dipole moments and energy curves are shown in Figs. 1 and 2. In these figures the dotted energy curves apply to the purely covalent and ionic states, whereas the solid curves represent the energies of the states resulting from the resonance. Immediately below are given dipole moment curves. In each case, for large internuclear separations the ionic moments approach the line $\mu = er$ asymptotically and the covalent moments approach zero.

In Fig. 1, the purely covalent energy is everywhere less than the ionic energy so that the moment associated with the normal state is everywhere less than $1/2(er)$ and the other moment greater than $1/2(er)$. In Fig. 2, the purely ionic curve cuts below the covalent curve, so that the moment of the normal molecule is greater than $1/2(er)$ for a certain range of r. The two moment curves cross with the value $1/2(er)$ at the same internuclear separation where the idealized energy curves cross. The case exhibited by Fig. 2 is to be expected for hydrogen fluoride.

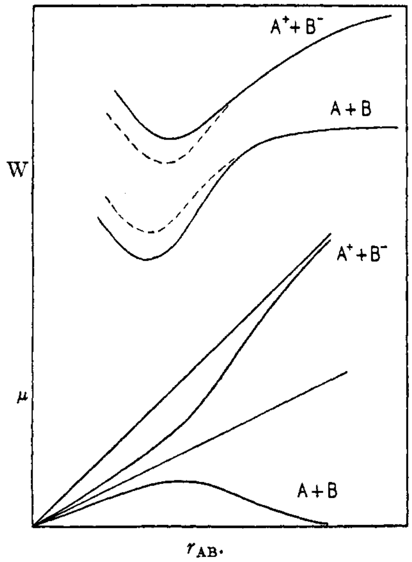

Fig. 1.—Energy and dipole moment curves with covalent state everywhere more stable than ionic state.

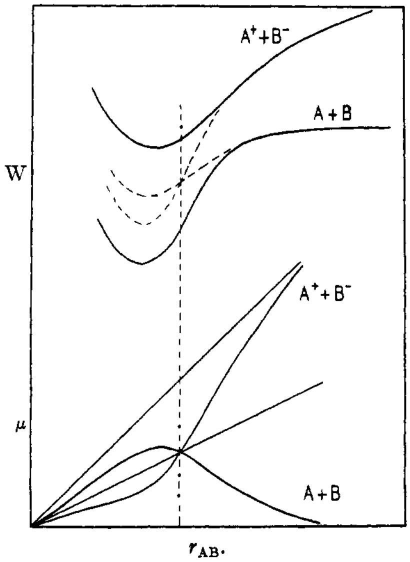

Fig. 2.—Energy and dipole moment curves with ionic state more stable than covalent state for certain range of internuclear separations.

The behavior of the moment curves for small internuclear separations is not certain, though it seems reasonable to suppose that the slopes are both different from zero for $r = 0$. At any place, of course, the sum of the slopes equals e by reason of equation (11). The two curves for the moments of the normal molecules were drawn to resemble those proposed by Mulliken.[5]

Since $0 \leqslant |\Delta| \leqslant 1$, it follows from equation (5) that a must lie in the range

$$\sqrt{\frac{\mu}{er - \mu}} \text{ to } \frac{\mu}{er - \mu}$$

From a knowledge of μ/er, one can then calculate upper and lower limits for $|a|$ for the normal molecules. The results of such calculations are given in Table I. Values of $|a|$ could of course be obtained for any value of Δ by use of equation (5). Such values have been calculated taking $\Delta = 0.3$, since it is likely that Δ is nearer 0 than it is to 1.

TABLE I

Molecule	μ/er	a values $\Delta = 0$	$\Delta = 0.3$	$\Delta = 1$	From energy data[2]
HF	0.60[a]	1.22	1.30	1.50	
HCl	.170	0.45	0.35	0.20	0.39
HBr	.114	.36	.25	.13	.35
HI	.049	.23	.13	.052	.26

[a] Value estimated by Pauling.[1]

In a previous paper,[2] values for a^2 were computed by means of energy data using equation (1). The corresponding values of $|a|$ except for hydrogen fluoride are shown in the last column of Table I. The energy curves used in those calculations were not very reliable, especially in the case of hydrogen fluoride, in which case they were way off. However, it is seen that the values for hydrogen chloride and hydrogen bromide calculated by the use of those energy curves lie between the upper and lower limits specified by dipole moment data. The value from energy curves for hydrogen iodide is a little higher than the upper limit from dipole moment data.

Since $a^2/(1 + a^2)$ might well be adopted as a measure of ionic character, values for that quantity are given in Table II for $\Delta = 0$, $\Delta = 0.3$ and $\Delta = 1$, as well as those values obtained from energy data. It should be noted that if $\Delta = 0$, then $a^2/(1 + a^2)$ is just μ/er. It is clear from the results in the tables that with increasing atomic number, a and $a^2/(1 + a^2)$ become increasingly sensitive to variations in Δ. It might well be that for hydrogen bromide and hydrogen iodide, Δ is nearer zero than 0.3.

TABLE II

Molecule	$a^2/(1 + a^2)$ $\Delta = 0$	$\Delta = 0.3$	$\Delta = 1$	From energy data[2]
HF	0.60	0.63	0.69	
HCl	.170	.11	.040	0.134
HBr	.114	.061	.016	.107
HI	.049	.016	.0026	.064

Summary

A theory of dipole moments of diatomic mole-

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(5) R. S. Mulliken, *J. Chem. Phys.*, **2**, 400 (1934).

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 resonating 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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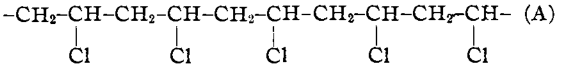
Removal of Substituents from Vinyl Polymers

BY FREDERICK T. WALL

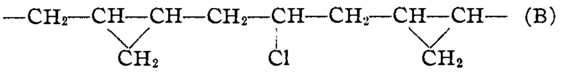
Experimental studies by Marvel and coworkers[1] have shown that chlorine can be partly removed from vinyl chloride polymers by means of zinc. The removal of chlorine is not quantitative, however, owing to the fact that some of the chlorides become isolated. A given chlorine atom is considered isolated 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


(A)

$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \quad (A)$$

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


(B)

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

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[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.