

gration current of a reducible ion by the preceding discharge of an uncharged substance (*e. g.*, oxygen) has been investigated. Experimental data are given to show that the accumulation of hydroxyl ions at the electrode surface, as a product of the reduction of oxygen, decreases the effective transference number (and hence the exaltation of the migration current) of the reducible ions.

3. It was found that the migration current of a reducible ion can also be increased by the preceding discharge of another reducible ion. The observed exaltation of the migration current of potassium ions by the preceding discharge of thallos ions was in good agreement with the calculated value.

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## Ionic Character in Diatomic Molecules

BY FREDERICK T. WALL

When one describes the normal state of a diatomic molecule such as a hydrogen halide, it is convenient to refer to it as being partly covalent and partly ionic in character.<sup>1</sup> Qualitatively, from dipole moment values, it is seen that the ionic character of the hydrogen halides decreases with increasing atomic number. However, no simple quantitative way has yet been proposed for estimating the relative contributions of ionic and covalent states to the normal state of a molecule. In this paper there will be shown a method whereby the relative importance of the two states can be estimated quantitatively from a knowledge of the actual potential energy curves and the idealized ionic and covalent curves.

Let us imagine a purely covalent state of a molecule with an electronic wave function  $\psi_c$  and also a purely ionic state with a wave function  $\psi_i$ . The wave function (unnormalized) for the actual molecule can then be approximated by

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

where  $a$  is a parameter dependent upon the relative importance of the two states. The energy of the system will be given by

$$W = \int \bar{\psi} H \psi d\tau / \int \bar{\psi} \psi d\tau \quad (1)$$

which upon expansion yields

$$W = \frac{H_{cc} + aH_{ci} + aH_{ic} + a^2H_{ii}}{1 + 2a\Delta + a^2} \quad (2)$$

where

$$\Delta = \int \bar{\psi}_c \psi_i d\tau = \int \bar{\psi}_i \psi_c d\tau$$

and

$$H_{ci} = \int \bar{\psi}_c H \psi_i d\tau, \text{ etc.}$$

Each of the quantities  $a$ ,  $\Delta$ ,  $H_{cc}$ ,  $H_{ic}$ ,  $H_{ci}$ ,  $H_{ii}$  and  $W$  will be dependent upon the internuclear

separation  $r$ .  $\Delta$  presumably goes to zero as the internuclear separation becomes large.

The actual energy of the molecule will then best be given by minimizing  $W$  with respect to the parameter  $a$ . Setting  $\partial W / \partial a = 0$ , there is obtained upon simplification

$$H_{ic} + H_{ci} = \frac{2(a + \Delta)H_{cc} - 2a(1 + a\Delta)H_{ii}}{1 - a^2} \quad (3)$$

Combining (3) with (2) there is obtained

$$W = (H_{cc} - a^2H_{ii}) / (1 - a^2) \quad (4)$$

since the term  $1 + 2a\Delta + a^2$  cancels out of both numerator and denominator. Solving for  $a^2$  from equation (4) we find

$$a^2 = (H_{cc} - W) / (H_{ii} - W) \quad (5)$$

Now  $H_{cc}$  and  $H_{ii}$  are, respectively, the energies which the molecule would have if it were in a purely covalent or a purely ionic state. Although such states are hypothetical, they are nevertheless frequently referred to in speaking of the molecules. Replacing  $H_{cc}$  by  $W_c$  and  $H_{ii}$  by  $W_i$ , the equation becomes

$$a^2 = (W_c - W) / (W_i - W) \quad (6)$$

**Empirical Evaluation of  $a$ .**—From equation (6) it is apparent that  $a$  could be determined as a function of  $r$  if we knew how  $W_c$ ,  $W_i$  and  $W$  depend upon  $r$ . Unfortunately curves for  $W_c$  and  $W_i$  cannot be produced with much certainty. However, an estimate of the value of  $a$  at the equilibrium internuclear separation can be made as follows. In accordance with the findings of Pauling and Sherman,<sup>2</sup> assume  $W_c$  for a molecule HX to be given by

$$W_c(\text{HX}) = \sqrt{W(\text{H}_2)W(\text{X}_2)} \quad (7)$$

(2) Linus Pauling and J. Sherman, *THIS JOURNAL*, **59**, 1450 (1937).

(1) Linus Pauling, *THIS JOURNAL*, **54**, 988 (1932).

where  $W(\text{H}_2)$  and  $W(\text{X}_2)$  are the known dissociation energies of hydrogen and the halogen considered. Then from the observed dissociation energy for the hydrogen halide,  $W_c - W$  can be calculated for the equilibrium internuclear separation.

The estimation of  $W_i - W$  is more difficult. It will be assumed here that

$$W_i = \frac{-e^2}{r} + \frac{B}{r^n} + I_H - E_X \quad (8)$$

where  $e^2/r$  is the ordinary coulomb term,  $B/r^n$  is a repulsive potential and  $I_H$  and  $E_X$  are, respectively, the ionization potential of hydrogen and the electron affinity of the halogen. The constant  $B$  can be eliminated from the expression by a knowledge of the ionic radius of the halogen.<sup>3</sup> In this case the radius used must be for the ion with unit coordination number, such a radius being less than the crystal radius. The radii used here were taken from a paper by Rodebush,<sup>4</sup> the values being rounded off because of their uncertainty.

By use of equation (8) the ionic energies at the normal covalent separations were calculated for the hydrogen halides using different sets of values for the repulsive exponent  $n$ . In accordance with the behavior of  $n$  in the case of crystals,<sup>3</sup> the repulsive exponents for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  were taken to exceed that of  $\text{F}^-$  by 1,  $1\frac{1}{2}$  and  $2\frac{1}{2}$  for each of the different sets.

The results are summarized in Table I. The numerical subscripts refer to the different sets of values for  $n$ . All of the energy values correspond

TABLE I

	HF	HCl	HBr	HI
$r_i$	1.1 Å.	1.5	1.6	1.8
$r_o$	0.93 Å.	1.28	1.42	1.62
$W$	-6.39 e. v.	-4.38	-3.74	-3.07
$W_c^a$	-3.53 e. v.	-3.31	-2.95	-2.61
$n_1$	2	3	3.5	4.5
$W_{i1}$	2.95 e. v.	3.45	3.60	4.09
$n_2$	4	5	5.5	6.5
$W_{i2}$	0.19 e. v.	2.53	2.85	3.66
$n_3$	6	7	7.5	8.5
$W_{i3}$	-0.24 e. v.	2.44	2.65	3.54
$W_o - W$	2.86 e. v.	1.07	0.79	0.46
$W_{i1} - W$	9.34 e. v.	7.83	7.34	7.16
$W_{i2} - W$	6.58 e. v.	6.91	6.59	6.73
$W_{i3} - W$	6.15 e. v.	6.82	6.39	6.61
$a_1^2$	0.306	0.137	0.108	0.064
$a_2^2$	.435	.155	.120	.068
$a_3^2$	.465	.157	.124	.070
$\mu/er_c$		.169	.116	.049

\* Calculated by use of equation (7).

(3) Jack Sherman, *Chem. Rev.*, **11**, 93 (1932).

(4) W. H. Rodebush, *Trans. Faraday Soc.*, **30**, 778 (1934).

to the covalent internuclear separation  $r_c$ . In the last row there are given values for  $\mu/er_c$  where  $\mu$  is the dipole moment of the molecule.

**Discussion of Results.**—It will be seen from the table that the calculated values of  $a^2$  do not vary a great deal for the different sets of  $n$  values, especially when  $n$  is large. It is probable that the second set of values is best, that set corresponding to a repulsive exponent of 4 for  $\text{F}^-$ . It is apparent that the ionic character, which is determined by  $a$ , decreases with increasing atomic number. In fact, the values of  $a^2$  are roughly equal to  $\mu/er_c$ . If  $\psi_i$  and  $\psi_c$  were orthogonal, we could write

$$\mu = \frac{a^2}{1 + a^2} er$$

assuming that the dipole moment is due entirely to the ionic contribution. However,  $\psi_i$  and  $\psi_c$  are actually not orthogonal, but it is still reasonable to suppose that the dipole moment will be approximately proportional to  $a^2$ , especially if  $a^2$  is small. In any case  $a$  equals the ratio of the coefficients of  $\psi_i$  and  $\psi_c$  for the actual wave function.

It is interesting to see when  $a^2$  will be maximum. The precise value of  $r$  corresponding to maximum  $a^2$  for the normal state cannot be found without more data or further assumptions. It is nevertheless clear that  $a^2$  will be a maximum in the neighborhood of the ionic radius or slightly beyond, since  $W_i - W$  reaches its smallest value somewhat beyond that radius. One would expect also that the dipole moment would have its maximum value for  $r$  approximately equal to or greater than the ionic radius. The dipole moment of the normal molecule must of course fall off to zero for infinite internuclear separation.

If the maximum value of the dipole moment occurs at a distance greater than the equilibrium separation, then  $(d\mu/dr)_{r=r_o} > 0$ . This is not in accordance with conclusions reached by Bartholomé<sup>5</sup> and by Bell and Coop.<sup>6</sup> It is possible, of course, that the moment is largely dependent upon cross terms such as  $\int \psi_c x \psi_i d\tau$ , which might make the dipole moment a maximum at much shorter distances. However, there seems to be no easy way of predicting the behavior of that integral.

In conclusion it should be noted that the methods employed here can be used for determining

(5) Bartholomé, *Z. physik. Chem.*, **B23**, 131 (1933).

(6) R. P. Bell and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1209 (1936).

the relative importance of two contributing states for molecules other than the hydrogen halides and for states other than ionic and covalent. Where the potential energy curves cross, however, complications are introduced by reason of resonance splitting at such crossing points due to perturbations.

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### Summary

Assuming the wave function of a molecule to be given by  $\psi = \psi_c + a\psi_i$  where  $\psi_c$  and  $\psi_i$  are covalent and ionic functions, respectively, the constant  $a$  is shown to be determined by

$$a^2 = (W_c - W)/(W_i - W)$$

Values for  $a^2$  are determined empirically and correlated with ionic character and dipole moment values.

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## Infrared Absorption of the Phenylmethanes

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Studies of the infrared absorption spectra of various organic molecules have shown that the molecules possess vibrational frequencies more or less characteristic of the bonds that occur in the molecule. Thus, two different molecules with a common group usually will give spectra each possessing bands representative of the group which is present in both molecules. This constancy of frequencies has proved highly useful in interpreting infrared absorption measurements, particularly where structural changes take place. This is possible because frequency shifts can be used as an indication of such changes.

With a view toward distinguishing spectroscopically between aliphatic and aromatic hydrogens, investigations were carried out for a number of hydrocarbons. In this paper there will be reported the results of studies on the phenylmethanes, which are the simplest molecules possessing both aromatic and aliphatic parts. In a subsequent paper, the results for a number of larger aromatic hydrocarbons will be given and the results correlated with the degree of aromatic character.

**Substances Used.**—The molecules here considered are benzene, toluene, diphenylmethane, triphenylmethane and tetraphenylmethane. Of these molecules, benzene<sup>1</sup> and toluene<sup>1,2</sup> have been carefully studied previously, but under conditions different from those present in the investigation here reported.

The benzene was Merck reagent benzene, thio-

phene free. A toluene sample was prepared by purifying technical toluene by the method of Schwalbe,<sup>3</sup> which removed thiophene and its homologs. The sample subsequently was fractionated and all but a limited portion discarded. The diphenylmethane and triphenylmethane were synthetic products prepared in the organic chemistry laboratories of the University of Illinois. The first three compounds were fractionated to constant boiling point and constant refractive index. For a sample of tetraphenylmethane we are indebted to Professor C. S. Schoepfle of the University of Michigan to whom we express our thanks. It was prepared from triphenylchloromethane and diphenylmagnesium and treated with concentrated sulfuric acid to remove traces of triphenylmethyl peroxide. It was then crystallized from benzene to give a product of high purity.

The absorption was studied for solutions of the substances in carbon tetrachloride by means of a technique previously described.<sup>4</sup> Except for tetraphenylmethane, the concentrations were kept constant at 0.1 molar and the cell length at 0.325 cm. A saturated solution of tetraphenylmethane was used in a 2-cm. cell. The instrument was a grating spectroscope of high resolution, the grating being of the echelette type with 3600 lines to an inch. A Nernst glower was used as a source of radiation. The absorption curves were investigated in the range 3.2 to 3.6  $\mu$ , which covers the region in which carbon-hydrogen vibrations are

(3) C. Schwalbe, *Ber.*, **38**, 2208 (1905).

(4) Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 501 (1937); Borst, Buswell and Rodebush, *ibid.*, **6**, 61 (1938).

(1) R. B. Barnes, *Phys. Rev.*, **36**, 296 (1930).

(2) C. E. Leberknight, *ibid.*, **43**, 967 (1933).