

A New Method of Calculating Resonance Energies

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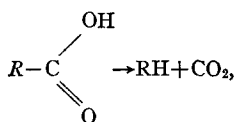
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TABLE I.

$\omega(\text{C}^{12})$	$\omega(\text{C}^{14})$	$\Delta\omega$	$G(u)$	$G(u)\Delta u$
Normal acid molecule				
1800	1713	87	0.343	0.107
837	834	3	0.219	0.002
493	490	3	0.140	0.002
1423	1346	77	0.301	0.083
483	481	2	0.138	0.001
700	659	41	0.180	0.029
				0.222
Activated complex				
1711	1633	78	0.332	0.093
1088	1053	35	0.260	0.032
				0.125

For the decarboxylation reaction of malonic and bromomalonic acids, investigated by Yankwich and Calvin,³ we take a model:



where R and OH are considered single particles. Experience with many normal vibration calculations⁵ indicates that for the stretching vibrations with zig-zag chains the distant heavy atoms have little effect. Thus we take effective masses of 16 for both OH and R. Although one might have preferred 17 for OH and 14 or 15 for R, the complication to the calculation seemed not worth while. The distant heavy atoms do effect bending vibrations, but inspection of the details of the rate calculations indicates that the net effect of these vibrations is much smaller than that of the stretching motions.

Taking force constants yielding approximately the observed frequencies of carboxylic acids, one then substitutes the mass 14 instead of 12 for the carboxyl carbon and calculates⁶ the frequencies of the "heavy" molecule. Selection of all details of the activated complex is less certain but it seems very likely that the C=O bond remains about normal. Since the R-C bond is being broken, its force constant is set to zero. Presumably the C-O bond has not yet become a double bond so it is given the same force constant as in the unreacted acid. Undoubtedly, the rigidity of bond angles is reduced in the activated state. Since the isotope effect on low frequencies is small anyway, all bending constants were set to zero. Thus there are just the C=O and the C-O vibrations in the activated complex model. All frequencies of the real molecule which the model omits are assumed to be unchanged by the isotopic substitution.

The calculated frequencies are given in Table I and apply equally to malonic or bromomalonic acid.

Bigeleisen has shown the ratio of rates for processes differing only isotopically to be

$$\frac{k}{k'} = \left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}} \left[1 + \sum_i \frac{3N-6}{G(u_i)\Delta u_i} - \sum_i \frac{3N-7}{G(u_i')\Delta u_i'}\right],$$

where $G(u)$ is the function defined by Bigeleisen and Mayer⁷ and $\mu = \hbar c \omega / k l$. The reaction coordinate reduced mass, μ , is taken as the reduced mass, $m_1 m_2 / (m_1 + m_2)$, associated with the atoms forming the bond being broken. The symbol ‡ refers to the activated complex. Table I shows the items in this calculation for the malonic acid reaction at 400°K.

The resulting calculated ratio of rates of breaking C¹²-C¹² to C¹²-C¹⁴ bonds is 1.14 as compared to the experimental 1.12 ± 0.03 for malonic acid and 1.4 ± 0.1 for bromomalonic acid. Bigeleisen's calculation yielded 1.04. Thus the present model accounts for the malonic acid results satisfactorily. The bromomalonic acid value comes from a single measurement internally less consistent than the others. If it should be confirmed, it will require a more drastic explanation.

The statistical rate theory⁸ makes the assumption that a full equilibrium concentration of activated complexes is maintained (remembering that these complexes have only positive velocities in the reaction coordinate). In a malonic acid with one C¹⁴ carboxyl group the C¹²-C¹² bond can break at a lower activation free energy than that required to break the C¹²-C¹⁴ bond. Now, if in the process of activation to the C¹²-C¹⁴ break, the molecule has a chance to react by the C¹²-C¹² break then this will tend to deplete the concentration of C¹²-C¹⁴ reacting complexes below the equilibrium value. This process would yield exceptionally high ratios of reaction rates.

The present model and standard statistical rate theory yield the same rate of C¹²-C¹² bond rupture in a C¹⁴ containing malonic acid as in the normal (all C¹²) molecule. However, if as postulated above, the rate of activation is not sufficient to maintain full equilibrium concentrations of activated complexes, then the double possibility of C¹²-C¹² bond rupture might deplete this concentration more in the normal molecule than the single possibility of C¹²-C¹² rupture does in the isotopic molecule. This point has not been checked experimentally in the malonic acid case but seems to arise in the behavior of the C₃H₈⁺ ion in the mass spectrometer.¹ Beeck and co-workers report that the C¹²-C¹² break is 7 percent more probable in a molecule with one C¹³ than in the normal molecule. The C¹³-C¹² break is 12 percent less probable than the normal C¹²-C¹² reaction.

Since the effective temperature of the propane ion in a mass spectrometer source is uncertain, no attempt will be made to carry analysis of that experiment further. The data² on the thermal cracking of propane-1-C¹³ at about 800°K show a higher ratio of rates than seems likely on a simple rate theory. However, details of the exact mechanism of this chain reaction are sufficiently uncertain to preclude further conclusions here.

¹ Beeck, Otvos, Stevenson, and Wagner, *J. Chem. Phys.* 16, 255 (1949).

² Stevenson, Wagner, Beeck and Otvos, *ibid.* 16, 993 (1948).

³ P. E. Yankwich and M. Calvin, *ibid.* 17, 109 (1949).

⁴ J. Bigeleisen, *ibid.* 17, 344, 425 (1949).

⁵ For example note the frequencies near 1000 cm⁻¹ in Fig. 2, *J. Chem. Phys.* 8, 714 (1940).

⁶ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand & Company, Inc., New York, 1945), pp. 179-180 and p. 174.

⁷ J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* 15, 261 (1947).

⁸ See Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

A New Method of Calculating Resonance Energies

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October 17, 1949

THE purpose of this note is to introduce a simple method for the approximate calculation of energies in molecules for which several reasonable electronic structures exist. The method is essentially a molecular orbital one in that the wave function for the system is written as the product of one-electron wave functions. Each such one-electron wave function is a molecular orbital (approximated as an LCAO) which has the characteristic of being centered on a single nucleus but which may be extended to include all nuclei adjacent to the central one.

To construct the MO's first write down all of the structures, I, II, III..., assumed to contribute to the ground state of the molecule. Each electron, or pair of electrons, in each structure is represented by a localized MO of the form $\psi = (1/\sqrt{2})(\psi_A + \psi_B)$ for an electron in a bond between nuclei A and B and $\psi = \psi_A$ for an electron on a single nucleus. (ψ_A and ψ_B are suitable, normalized atomic orbitals.) The complete MO centered on nucleus A is now obtained by taking a linear sum of all of the localized MO's involving nucleus A. This is done with due regard for the contribution of each structure to the ground state.

$$\psi(A) = a\psi_I(A) + b\psi_{II}(A) + c\psi_{III}(A) \dots \quad (1)$$

Each complete *MO* so constructed holds on the average zero, one, or two electrons, the number being uniquely determined by the structures used. (A pair of electrons in a bond can be considered as one electron on each nucleus or two electrons on one nucleus and none on the other. However, if any of the structures used show a nucleus with no electrons, or one or two unpaired electrons, then the *MO* constructed on that nucleus must have the same electron population in all structures.)

The coefficients $a, b, c \dots$ above can be found by solving the secular equation

$$\begin{vmatrix} H_{II} - W & H_{II} - \Delta_{II} W \dots \\ H_{II} - \Delta_{II} W & \dots \end{vmatrix} = 0, \quad (2)$$

where since the total electronic energy is to be a minimum, H_{II} is the sum of the electronic energies in structure I , each calculated in terms of Coulombic integral q and exchange integral β by the usual simplified *MO* method. H_{II} is the sum of the electronic energies calculated, for example, for an electron in the *MO* centered on nucleus A :

$$H'_{II} = \int \psi_I(A) H' \psi_{II}(A) d\tau \quad (3)$$

where H' is a single electron Hamiltonian. Δ_{II} is the average value of the overlap integral Δ'_{II}

$$\Delta'_{II} = \int \psi_I(A) \psi_{II}(A) d\tau \quad (4)$$

for each *MO* weighted according to its population. The lowest root of (2) then gives the values of $a, b, c \dots$ which make the total energy of the system a minimum.

This method in general gives excellent agreement with ground state energies calculated by either the usual *MO* method or the valence bond method and is frequently simpler to use. It has the advantage for chemists of emphasizing conventional bond structures while retaining the simplicity of *MO* calculations.

As an example, calculate the energy of the six π -electrons of benzene considering only the two Kekulé structures. (For simplicity but not by necessity the usual assumptions as to orthogonality and exchange integrals between non-adjacent atoms will be made.) The secular equation calculated by the rules given above is

$$\begin{vmatrix} 6q+6\beta-W & 3q+6\beta-\frac{W}{2} \\ 3q+6\beta-\frac{W}{2} & 6q+6\beta-W \end{vmatrix} = 0 \quad (5)$$

which has the lowest root $W = 6q + 8\beta$. The six complete molecular orbitals centered on each carbon nucleus are all equivalent and of the form $\psi(B) = 1/(6)^{1/2}(2\psi_B + \psi_A + \psi_C)$, etc. Each has an average population of one electron with an energy of $q + 4/3\beta$. It is of interest to note that the inclusion of the Dewar structures of benzene does not improve the energy; in fact, they make no contribution in this method of calculation.

A One-Dimensional Treatment of the Hydrogen Molecule Ion

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October 8, 1949

THE Pauling treatment¹ of the H_2^+ leads to the energy expression

$$E = W_H + e^2/R_{ab} + (J + K)/(1 + \Delta),$$

where

$$J = \int \frac{U_{1a}U_{1a}d\tau}{r_b},$$

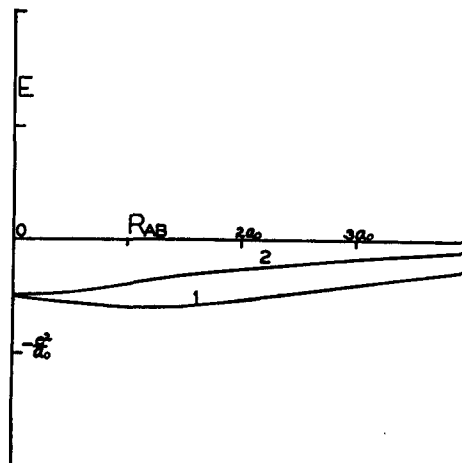


FIG. 1. $K/1 + \Delta$. (1) for the one-dimensional model, (2) for the three-dimensional model.

$$K = \int \frac{U_{1a}U_{1b}d\tau}{r_b},$$

$$\Delta = \int U_{1a}U_{1b}d\tau.$$

This treatment yields a binding energy for H_2^+ of $0.384e^2/a_0$ compared with the experimental $0.603e^2/a_0$.

One of the reasons for the low result is the lack of polarization in the atomic wave functions. It was of interest, therefore, to ascertain the effect of 100 percent polarization, i.e., the restriction of the motion of the electron along the axis of the molecule. The exchange integral $K/1 + \Delta$ can be evaluated for this model although the Coulomb integral $J/1 + \Delta$ cannot.

The one-dimensional hydrogen atom Schrodinger equation² is

$$d^2\psi/dx^2 + (8\pi^2M)/h^2(W + e^2/|x|)\psi = 0$$

with solution $\psi = (2/a_0)^{1/2}|x| \exp -|x|/a_0$ corresponding to the ground state energy, $W_H = 0.5e^2/a_0$. The expression for $K/(1 + \Delta)$ in units of e^2/a_0 becomes

$$\frac{-(R^2 + R + 1)e^{-R}}{1 + (R^3/3 + R + 1)e^{-R}},$$

where $R = (R_{ab})/a_0$. As is expected, the value of $K/1 + \Delta$ is larger for the one-dimensional (100 percent polarized) model than for the three-dimensional model (see Fig. 1). Combining the former with the three-dimensional $J/1 + \Delta$ the binding energy is 37 percent greater than the exact value.

¹ L. Pauling, Chem. Rev. 5, 173 (1928); L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 327.

² V. R. Vrikljan, Zeits. f. Physik. 52, 735 (1927).

The Transport Properties for Non-Polar Gases

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October 17, 1949

OUR attention has just been called to the work of T. Kihara and M. Kotani on the determination of intermolecular forces from transport phenomena in gases.¹

In this article Kihara and Kotani performed essentially the same integrations as we did² to obtain the Chapman and Coeling collision integrals for non-polar gases using the Lennard-Jones potential, with an inverse twelfth power energy of repulsion and an inverse sixth power energy of attraction.