

Carbon Isotope Effect on Reaction Rates

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† Lieutenant Colonel, U. S. Army, now stationed at Walter Reed Hospital, Washington, D. C.

¹ G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.* **20**, 585 (1948).

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Decrease of an Electrical Discharge by External Radiation: Joshi-Effect

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October 17, 1949

THE letter entitled "Decrease of an Electrical Discharge by External Radiation" by R. Parshad and S. Karim¹ in a recent issue of the Journal implies the claim that some new phenomenon has been observed by the authors. But there can be no doubt that what they have observed is the now well-known negative Joshi-Effect predicted and discovered by Professor Joshi, Benares, as early as 1938.^{1a} The Effect consists in an instantaneous and reversible photo-variation, usually diminution, of the discharge current when a number of gases and their mixtures, e.g., Cl₂, H₂, O₂, air etc. as well as metallic vapors, e.g., Hg, K, Se etc. and organic substances are subjected to electrical discharge and irradiated by visible, ultraviolet or x-rays. The Effect has been observed in full and semi-ozonizers as well as in Geissler tubes fitted with internal² or sleeve electrodes.³ This phenomenon has been the subject of extensive investigation in these laboratories and elsewhere since 1938 and the literature on the subject is already considerable. It is of interest to recall that R. Parshad himself has contributed two notes on the subject,⁴ wherein he has attempted to formulate a theory explaining the origin of the Effect. It may, however, be added that results obtained in these laboratories are not in accord with Parshad's theory.

Attention may be drawn to K. R. Dixit's letter⁵ wherein he has critically examined the problem of the Joshi-Effect and offered suggestions for further experimental work. Working at Professor Joshi's suggestion, Ramana Rao² has studied the Joshi-Effect in air and chlorine subjected to Geissler discharge and observed the transition from negative Joshi-Effect at low applied potentials to positive Effect at high potentials. Again, Joshi-Effect of large magnitude, viz., 90–100 percent current suppression by external radiation by visible light has been observed in chlorine,⁶ and in air,⁷ especially with the ozonizer walls coated with KCl. It is hence incomprehensible that Parshad and Karim should make no reference to the Joshi-Effect and to the spectral observations of P. G. Deo⁸ on the emission spectrum of Cl₂, of K. V. Rao⁹ and of Venkateswarlu¹⁰ on the absorption spectrum of iodine vapor and mercury vapor respectively, under conditions when all the systems under excitation showed large Joshi-Effect, and especially to the general conclusion that an "adsorption-like electrode layer" represents the seat of the phenomenon.

¹ R. Parshad and S. Karim, *J. Chem. Phys.* **17**, 667 (1949).

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⁸ P. G. Deo, *Phil. Mag.* **39**, 978 (1948).

⁹ K. V. Rao, *Proc. Ind. Acad. Sci.* **29**, 211 (1949).

¹⁰ V. Venkateswarlu, *Proc. Ind. Sci. Cong.* (1949), *Phys. Sec., Abst.* **35**.

Diamagnetic Anisotropy of *p*-Polyphenyls

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October 28, 1949

IN a note published some time ago in this Journal,¹ Brooks has shown how London's calculations² of the diamagnetic anisotropy of various unsaturated aromatic molecules may be modified in order to allow for non-orthogonality between the atomic (*2p*)-orbitals on adjacent atoms. Although the modification of London's results is quite small for most of the molecules considered, diphenyl appears to provide a remarkable exception to the rule, the implication being that any agreements between experiment and theory are largely fortuitous. In an application of London's method to the *p*-polyphenyls C_{6n}H_{4n+2}, *n* = 2, 3, 4, ..., it was necessary to check previous calculations, with the following results.

(i) The energy level $x = 0.070,5$ quoted from London's paper by Brooks, is too small by a factor of 10 (printer's error). On using the correct value the anomaly mentioned above no longer exists.

(ii) A numerical error in London's calculations (contribution to the susceptibility from electrons in the level $x = 1.317,4$) completely invalidates his final result.

(iii) In terms of $\Delta\chi_{\text{benzene}}$ the following corrected results have been obtained

$$\Delta\chi_{\text{diphenyl}} = 1.869,5\Delta\chi_{\text{benzene}} \text{ (without overlap),}$$

$$\Delta\chi_{\text{diphenyl}} = 1.966,7\Delta\chi_{\text{benzene}} \text{ (with overlap integral } S = 0.25).$$

These figures may be compared with London's result,

$$\Delta\chi_{\text{diphenyl}} = 2.21\Delta\chi_{\text{benzene}} \text{ (without overlap).}$$

Whereas London's calculations suggest that conjugation across the connecting link in diphenyl would raise the susceptibility normal to the plane, our results indicate an exactly opposite effect, the fusion of two benzene rings in this manner leading to a decrease in their net susceptibility.

This result is not significantly altered if one makes allowance for the change in ring size due to conjugation: Moreover, calculations which will be fully reported in due course predict the maintenance of this trend in higher members of the series, the diamagnetic anisotropy of the *n* rings in a *p*-polyphenyl continuing to fall below that of *n* independent (coplanar) rings.

Although a quantitative agreement with experimental data cannot be anticipated, one might expect to find experimental evidence for a trend of this kind. In fact, the very limited data available³ does not appear to support our conclusions. In view, however, of the indirect nature of the experimental determinations, and in particular of the uncertainty in $\Delta\chi_{\text{benzene}}$, the disagreement should not, we feel, be regarded as conclusive.

¹ H. Brooks, *J. Chem. Phys.* **9**, 463 (1941).

² F. London, *J. de phys. et. rad.* **8**, 397 (1937).

³ Lonsdale, *Proc. Roy. Soc.* **A159**, 149.

Carbon Isotope Effect on Reaction Rates

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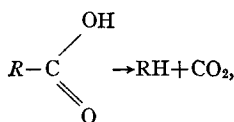
October 10, 1949

RECENT experiments¹⁻³ have shown surprisingly large effects on reaction rates with the substitution of carbon 13 or 14. Bigelseisen⁴ has discussed these results in terms of statistical rate theory. While his fundamental theory and formulas are sound, the writer believes his choice of simplified model for one of the molecules can be improved. The possible interpretation will also be discussed for cases where agreement with simple statistical rate theory cannot be obtained.

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 $u = h\omega/kT$. The reaction coordinate reduced mass, μ , is taken as the reduced mass, $m_1m_2/(m_1+m_2)$, 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.

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