We now report the first measurement of the rate constant (k) of the interconversion of Ia and Ib. This has been achieved by observing the C^{13} satellites[4] of the main line[5] of the high-resolution proton nuclear magnetic resonance (n.m.r.) spectrum of I over temperatures ranging from −55° to room temperature (Fig. 1).[6]

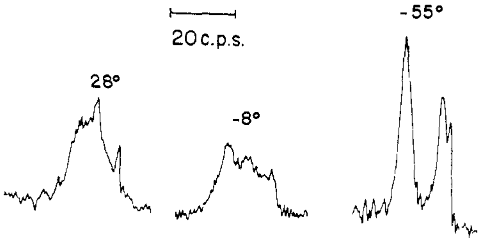

Fig. 1. High-field C^{13} satellite of cycloöctatetraene in carbon disulfide solution (2:1) at various temperatures. The low-field satellite was always a mirror image of the high field one. The spectra were measured on a 60 Mc./sec. Varian spectrometer. The magnetic field increases from left to right.

At low temperatures, when k is very small, Ia and Ib will be observable[7] as separate species. The proton on a C^{13} atom (say H1 of Ia) would be expected to be coupled to H2 by about 12 cps. (*i.e.*, normal *cis*-coupling[8] on a double bond). Although H2 is not chemically shifted from H3 it is not expected to be appreciably coupled to H3 because[9] the dihedral angle between the planes defined by H2,C2,C3 and H3,C3,C2 is about 90°. For the same reason H1 should not be coupled to H8. Therefore, H1 should give a doublet with a separation of about 12 cps., and H2, H3, *etc.*, whether in Ia or Ib should also give the same type of doublet when attached to C^{13} atoms. The C^{13} satellites of I at −55° (Fig. 1) are indeed doublets with a separation of 11.8 cps. The components of the doublet show additional but small splittings which can be ascribed to long-range coupling and/or not quite zero coupling the H1, H8 type.

At higher temperatures, when k is very large, only the average of Ia and Ib will be observed.[7] The spectrum (say when C1 is a C^{13} atom) would now be expected to be very complicated. The protons in the pairs (H1,H2), (H2,H3), (H3,H4), *etc.*, should be coupled together by about 6 cps. (*i.e.*, the average of 12 and zero), but since there is zero chemical shift between H2,H3 ... H8, to be completely correct, the spectrum has to be analyzed as an eight-spin system. If H2 and H8 only are taken into account, then H1 would be expected to be a 1:2:1 triplet with a spacing of about 6 cps., but this is undoubtedly a crude approximation. With the inclusion of H3 and H7 and only 1,2 coupling assumed, H1 forms the X part of two separate ABX systems and is calculated to be approximately a 1:3:4:3:1 quintet with a spacing of about 3 cps. The true spectrum will contain still more lines, which probably will result in an unresolved broad band, although some fine structure may remain. The shape of the C^{13} satellite of I at room temperature (Fig. 1) fits very well with these expectations.

As the temperature is raised from −55°, little change in the C^{13} satellites is observed until about −25°, when both components of the doublet begin to broaden rapidly. At about −10° only a single flat band (Fig. 1) is obtained and by about +5° the band shape has become constant and is the same as observed at room temperature. The rate constant at about −10° is[7] of the order of magnitude of the averaging effect on the doublet found at low temperatures. This gives a value of about 26 sec.$^{-1}$ for k, and about 13.7 kcal./mole for the free energy of activation at −10°.

Unfortunately, the spectra are not suitable for directly obtaining accurate activation energies. If the entropy of activation is assumed to be zero, then ΔH is about 13.7 kcal./mole. This is probably a maximum value for the difference in energy between the planar and tub forms of I. Although it is difficult to estimate the strain energy in the planar form, a value[10] of 20–30 kcal./mole would seem reasonable. Thus the resonance energy in the planar form amounts to not more than 5–15 kcal./mole, in agreement with the theoretical deductions.[3]

---

[4] A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

[5] Since all the protons of Ia and Ib have the same chemical shift, the main spectrum of I is a single line which does not change with temperature, and therefore cannot give any information about k.

[6] After submission of this paper, Dr. J. D. Roberts informed us that similar observations of the effect of temperature on the C^{13} satellites of cycloöctatetraene have been made in independent, unpublished research by G. M. Whitesides and J. D. Roberts at the California Institute of Technology.

[7] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959, p. 218.

[8] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 85.

[9] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[10] See F. H. Westheimer in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y. p. 533.

[11] This work was supported by a grant from the Ontario Research Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OTTAWA
OTTAWA, ONT., CANADA
F. A. L. ANET[11]

RECEIVED NOVEMBER 18, 1961

EVIDENCE FOR PHOTOCHEMICAL SPACE INTERMITTENCY EFFECT

Sir:

If a solution is illuminated with a pattern of light and dark areas and if photochemically produced fragments are destroyed in pairs, then the average steady-state concentration of fragments is dependent upon the size and shape of illuminated regions as well as upon the total area illuminated. The theory of this photochemical space intermittency effect has been examined previously.[1] We have now obtained an experimental demonstration of its existence.

The solution contained 1.0 × 10^{-4} M iodine in hexane illuminated at 25° with the 4358 Å. mercury line. Illuminating light fell on the solution

---

[1] R. M. Noyes, *J. Am. Chem. Soc.*, **81**, 566 (1959).

in a "leopard" pattern such that the distance from the center of a spot to each of its six nearest neighbors was three times the diameter of the spot. Patterns for transmitting the light were kindly prepared by the Research Laboratories of the Eastman Kodak Company by photographing a master pattern at different distances with high contrast emulsion. The cell containing the solution was only 5 mm. thick to reduce light scattering, and the light traversed this cell vertically to reduce convection effects. Intensity of illumination in a spot and total area illuminated were the same in all experiments.

The average concentration of iodine atoms in the cell was determined by measuring the rate of isotopic exchange with *trans*-diiodoethylene.[2] Figure 1 shows a plot of relative atom concentration against log r_L where r_L is the radius of an illuminated spot. One anomalously low measurement at very small spot radius has been omitted from the plot.

The dashed horizontal lines denote the theoretical limits for large and small spots computed from measurements with homogeneous illumination at the same intensity as the local intensity in the spots. The curve illustrates the theoretical predictions of reference 1 in terms of ρ_L, the spot radius in units of the magnitude of the root-mean-square diffusion distance for an atom during its lifetime in a homogeneously illuminated solution. The curve has been shifted horizontally to provide a fit to the experimental points, this fit being such that ρ_L of unity corresponds to $r_L = 0.0040$ cm.

The theoretical analysis[1] predicts that

$$\rho_L = (4\phi q k/D^2)^{1/4} r_L \qquad (1)$$

where q = rate of absorption of radiation in an illuminated area = 7.71×10^{-10} einstein/liter sec., ϕ = quantum yield for iodine dissociation = 0.66,[3] and k = rate constant for iodine atom recombination = 1.3×10^{10} liter/mole sec.[4] Then D, the diffusion coefficient for iodine atoms in hexane, becomes 8.2×10^{-5} cm.^{2}/sec.

This result is more than the value of 4.05×10^{-5} cm.^{2}/sec. reported[5] for iodine molecules. It is also somewhat more than the 5.3×10^{-5} cm.^{2}/sec. diffusion coefficient of iodine atoms predicted if the theory of diffusion controlled reactions in an isotropic medium[6] is applied to the observed[4] rate constant for iodine atoms of assumed diameter[7] 4.30 Å. Shifting the curve in Fig. 1 by 0.09 unit to the left would bring it into agreement with the predictions of the isotropic medium theory.

The experimental observations provide only a fair fit to the theoretical curve. At very large spot size, the concentration of isotopically labelled I_2 could become locally depleted. This effect can be corrected for and may be responsible for the one point below the theoretical minimum. At small spot size, any fuzziness of the boundary will make the average atom concentration greater than that predicted by the theory developed for a sharp boundary. This effect probably is responsible for the fact that the points in Fig. 1 rise more steeply than the theoretical curve, and such a steep rise makes the calculated diffusion coefficient larger than the true value. The theory of this diffuse boundary effect must be developed.

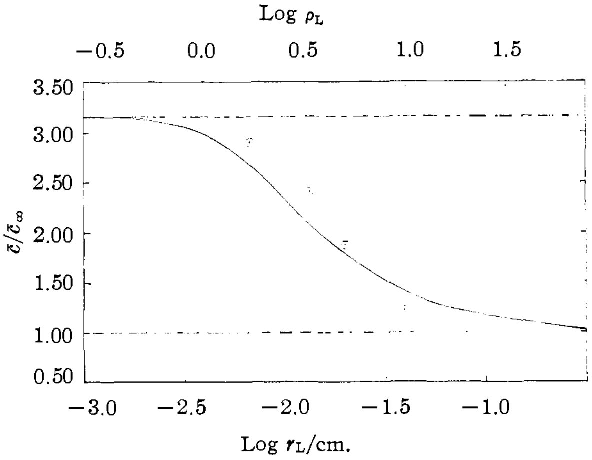

Fig. 1.—Ratio of average iodine atom concentration, $\bar{c}$, to average predicted for very large spots, $\bar{c}_\infty$. Measurements were made with same total intensity of illumination but different sizes of individual spots.

Although the method must be refined before it is possible to measure diffusion coefficients much more accurately than to about a factor of two, these results demonstrate unequivocally that at constant total illumination of a solution the average concentration of radicals increases with decrease in size of the individual illuminated areas and that the effect is of the magnitude predicted by the previously developed theory.

This work was supported in part by the U. S. Atomic Energy Commission under Contract AT-(45-1)-1310.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON
G. A. SALMON
RICHARD M. NOYES

RECEIVED DECEMBER 11, 1961

---

[2] J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

[3] F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

[4] H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

[5] R. H. Stokes, P. J. Dunlop, and J. R. Hall, *Trans. Faraday Soc.*, **49**, 886 (1953).

[6] R. M. Noyes, "Progress in Reaction Kinetics," Pergamon Press, Oxford, England, Volume I, 1961, p. 136.

[7] L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N. Y., 1960, p. 260.

REPORTING NUCLEAR MAGNETIC RESONANCE SHIELDING DATA

Sir:

Nuclear magnetic resonance spectral data are at present reported in a variety of units. This communication is not an endorsement of any particular one but instead points out certain incorrect usage.

In some current journals, *tau* (τ) values have been used to report positions of lines which were a part of spin multiplets[1] and coupling constants have been

---

[1] E. C. Taylor, W. W. Paudler, and I. Kuntz, Jr., *J. Am. Chem. Soc.*, **83**, 2967 (1961); W. R. Brasen and R. E. Benson, *ibid.*, **83**, 3135 (1961); F. Marki, A. V. Robertson, and B. Witkop, *ibid.*, **83**, 3341