

inductive effect is obscured by concurrent conjugative effects.

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Tritiodeprotonation of Biphenylene¹

Sir:

Because of its unique structure, biphenylene has been of considerable chemical and theoretical interest for some years.² The molecular orbital prediction³ that the 2-position is the more reactive has been confirmed by repeated observations of exclusive reaction at the 2-position by several electrophilic substitutions: nitration, halogenation, acylation, mercuration, etc.^{2,4} No data have been available hitherto relating to the important question of the quantitative relative reactivities of the 1- and 2-positions. We now wish to report the rates of tritiodeprotonation for both the 1- and 2-positions of biphenylene.

The exchange medium, tritiated trifluoroacetic acid-70% perchloric acid (96.9:3.1 by volume), is similar to that used by Eaborn and Taylor⁵ in their studies of detritiation of tritiated aromatic hydrocarbons. Biphenylene undergoes progressive decomposition to tars after long reaction times; hence, the biphenylene was isolated from each kinetic aliquot by sublimation and its purity was monitored by g.c. analysis before counting on a Nuclear-Chicago Model 724 liquid scintillation counter. The kinetic problem is that of two parallel and reversible first-order reactions. The total specific activity at equilibrium is the sum of the activity of the 1- and 2-positions; therefore, a plot of $\log(DPM_{\infty} - DPM_t)$ vs. time gives a curved plot (Fig. 1) correspond-

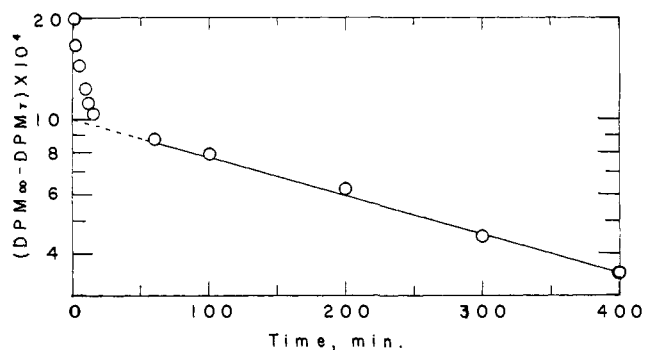


Fig. 1.—Kinetic run for tritiodeprotonation of biphenylene at 25°.

ing to the two different reactions. After the first reaction has reached equilibrium, the points representing the slower reaction (presumed to be α) can be extrapolated back to zero time. The value of $DPM_{t=0}$ should be half that of DPM_{∞} , and this value, as well as corrected DPM_t values, can be used to ascertain the rate of the faster reaction (presumed to be β) as shown in Fig. 2.

(1) This research was supported in part by a grant from the United States Air Force Office of Scientific Research of the Air Research and Development Command.

(2) The chemistry of biphenylene has been reviewed recently by W. Baker and J. F. W. McOmie in D. Ginsburg's "Non-benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959.

(3) R. D. Brown, *Trans Faraday Soc.*, **46**, 146 (1950).

(4) W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); W. Baker, J. W. Barton, and J. F. W. McOmie, *ibid.*, 2658, 2666 (1959); W. Baker, J. F. W. McOmie, D. R. Preston, and V. Rogers, *ibid.*, 414 (1960).

(5) C. Eaborn and R. Taylor, *ibid.*, 1012 (1961);

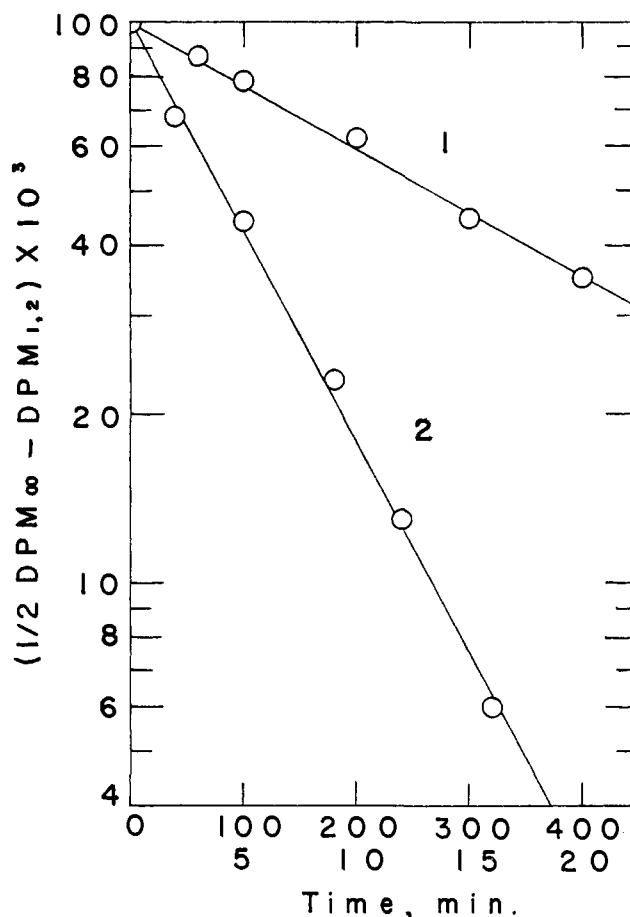


Fig. 2.—Analysis of kinetic run into simultaneous first-order reactions for the 1- and 2-positions of biphenylene. The bottom time scale is for the 2-position.

This method was applied to naphthalene and gave rate constants of 3.4×10^{-4} and 5.6×10^{-5} sec.⁻¹. The ratio of rates (6.1) is virtually identical with that obtained by Eaborn and Taylor⁵ ($k_{\alpha} = 5.3 \times 10^{-4}$ sec.⁻¹; $k_{\beta} = 8.85 \times 10^{-5}$ sec.⁻¹) and similar to that (7.6) obtained by Dallinga, *et al.*,⁶ for $CF_3COOD-D_2SO_4-CCl_4$. Biphenylene gave $k_{\alpha} = 4.32 \times 10^{-5}$ sec.⁻¹ and $k_{\beta} = 2.75 \times 10^{-3}$ sec.⁻¹; $k_{\beta}/k_{\alpha} = 64$. This ratio, which has also been confirmed by detritiation of specifically labeled biphenylenes, agrees qualitatively with various molecular orbital predictions but is in serious quantitative disagreement. Localization energies, for example, predict $k_{\beta}/k_{\alpha} \approx 4$.⁷ This limitation in an important quantitative application of simple molecular orbital theory is, furthermore, not significantly improved by introduction of the ω -technique.

(6) G. Dallinga, A. A. V. Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).

(7) See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961. Chapter 11.

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^N14 and ^C13 Nuclear Magnetic Resonance Studies of Iron Hexacyanides

Sir:

This communication reports some results obtained in a ^C13 and ^N14 n.m.r. study of potassium ferricyanide ($K_3Fe(CN)_6$) and potassium ferrocyanide ($K_4Fe(CN)_6$) in aqueous solutions. The ferricyanide is paramagnetic and the magnetic susceptibility of its aqueous solution

TABLE I

$K_4Fe(CN)_6$		$K_3Fe(CN)_6$		Chemical shift	Temperature dependence $K_3Fe(CN)_6$ (10–80°)
Position	Width ^a	Position	Width ^a		
-0.7 ± 0.3^b	3.0 ± 0.2	-11.6 ± 0.2^b	2.5 ± 0.2	10.9 ± 0.2	$+3.3 \times 10^3$ gauss deg.
$+0.9 \pm 0.5^c$	$+50 \pm 0.50^c$	49.2 ± 0.4	-13.7×10^3 gauss deg.

^a Extrapolated to zero concentration. ^b Relative to N^{14} in pure CH_3CN ; 32°. ^c Relative to C^{13} in pure C_6H_6 ; 32°.

is known,¹ while the ferrocyanide is diamagnetic. The measurements of the chemical shifts might lead to evaluation of the spin density distribution in the paramagnetic ion and from the line widths the mechanism and kinetics of the electron exchange between the para- and diamagnetic species can be determined. The position and width of N^{14} resonance in solutions of $K_3Fe(CN)_6$ were previously measured by Shulman² and his results are in fair agreement with ours. Shulman attributes the paramagnetic shift to anisotropic hyperfine interaction.

The N^{14} and C^{13} line positions and widths of approximately 0.5 *M* aqueous solutions of the pure compounds are given in Table I. Results are expressed in gauss, and measured in a magnetic field (H_0) of about 14 kgauss. A bulk susceptibility correction was not applied since calculation shows it to be rather small (less than the line width). Shifts to a higher magnetic field are indicated as positive. The position of the N^{14} and C^{13} resonances in the paramagnetic species is a linear function of the reciprocal of the absolute temperature and the slope is given in the last column of Table I.

The results in Table I indicate: (1) The line width of N^{14} in $K_3Fe(CN)_6$ is smaller than in $K_4Fe(CN)_6$, which means that it is completely determined by quadrupolar relaxation, since, otherwise, one would expect additional broadening due to the unpaired electron in $K_3Fe(CN)_6$. The electrical field gradient at the N nucleus seems to be larger in $K_4Fe(CN)_6$, which might be attributed either to its stronger complexation with counter-ions,³ which affects the symmetry of the ion, or to the higher total charge of the anion. (2) Relative to line positions in the diamagnetic species, N^{14} resonance in $K_3Fe(CN)_6$ is shifted to lower field while the C^{13} resonance is shifted, considerably more, to higher field. Calculation of the hyperfine coupling constants A_i from the contact shifts⁴ gives $A_{N^{14}} = 0.78$ gauss and $A_{C^{13}} = -11.8$ gauss (taking $g = 2$ and $S = 1/2$). Assuming equal signs and similar magnitudes of the Q -values in the expression $A_i = Q\rho_i$, we deduct that the spin density of the C^{13} would be approximately 15 times higher than on the N^{14} with opposite signs. The linear dependence of C^{13} and N^{14} resonances on the reciprocal absolute temperature shows that the shift is mainly due to the unpaired electron (paramagnetic shift).

In aqueous solutions of mixtures of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, one N^{14} resonance is observed; hence, the electron exchange rate is fast compared to the reciprocal of the chemical shift. The line width is dependent on the concentration of the ferri- and ferrocyanide. At constant total concentration maximum width is obtained in approximately 1:1 mixtures. The position of the common line is a linear function of the mole fraction of the ferri- and ferro- in the mixture. The rate of electron exchange was evaluated from the measured line width using the fast exchange approximation for an unequal doublet with different "natural" T_2 values.⁵ Assuming the reaction to be described by:

rate = $k[Fe(CN)_6^{-4}][Fe(CN)_6^{-3}]$, the value of k was found to be $(6.0 \pm 0.7) \times 10^4$ sec.⁻¹ *M*⁻¹ at 32°. The range of ferri- and ferrocyanide concentrations used was 0.3–0.6 *M*; the error given is the standard deviation from 14 measurements. No analogous measurements with C^{13} line width were obtained because of the low *S/N* ratio. The rate constant obtained is in fair agreement with that obtained by Wahl and co-workers,^{3,6} who studied the electron exchange by isotope labeling techniques. The advantage of n.m.r. in this study is obvious, in view of the elimination of the uncertainty in the "zero-time exchange" occurring with the isotope labeling technique,⁶ while the disadvantage lies in the high concentrations that must be used. The catalytic effects of various alkali positive ions on the exchange and the temperature dependence of the reaction are presently under study.

Measurements were performed on a Varian DP60 spectrometer equipped with a V4311 4.3-Mc. fixed frequency unit for N^{14} measurements and a V4210A variable frequency unit operating at 15.0 Mc. for C^{13} measurements. Samples were contained in 15-mm. o.d. tubes. In temperature dependence studies 8 mm. o.d. tubes were used in a specially constructed dewar insert. For some C^{13} measurements $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ were prepared from C^{13} -enriched⁷ KCN by a procedure similar to that given by Thompson.⁸

(6) A. C. Wahl, *Z. Elektrochem.*, **64**, 90 (1960).

(7) The authors wish to thank Professor G. Stein of the Hebrew University, Jerusalem, for kindly providing KCN enriched to 15 atom % C^{13} .

(8) R. C. Thompson, *J. Am. Chem. Soc.*, **70**, 1045 (1948).

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Long-Range Spin-Spin Coupling of Protons in Isomeric 6,7-Dichloroestrone Methyl Ethers

Sir:

Spin-spin coupling of protons, attached to carbon atoms two or more bonds apart, has been observed in a number of systems containing unsaturation.¹ The success of theoretical treatments of such unsaturated systems² is evident from the verification of some of their predictions by experiments.¹ The theory of spin-spin splitting does not provide a reliable basis for the prediction of long-range spin-spin coupling in saturated systems.³

We have observed a strong spin-spin coupling between protons attached to carbon atoms two σ -bonds

(1) For leading references, see (a) E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962); (b) D. J. Collins, J. J. Hobbs, and S. Sternhell, *Tetrahedron Letters*, 197 (1963); (c) T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1699 (1963); (d) J. R. Holmes and D. Kivelson, *ibid.*, **83**, 2959 (1961); (e) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963); (f) E. W. Garbisch in Abstracts of Papers presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 36Q; ref. 7f and earlier references cited therein.

(2) (a) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); (b) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958), and subsequent papers, see ref. 1a; (c) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

(3) (a) See ref. 1a, footnote 6; (b) D. R. Davies and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2252 (1962); (c) F. A. L. Anet, *ibid.*, **84**, 747 (1962); (d) K. B. Wiberg, B. R. Lowry, and B. G. Nist, *ibid.*, **84**, 1594 (1962); (e) J. Meinwald and V. C. Meinwald, *ibid.*, **85**, 2514 (1963), and earlier references cited therein; (f) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962), have developed the theory of "virtual" long range spin-spin coupling, which does not apply to the findings reported by us, see footnote 9.

(1) F. W. Gray and W. M. Birse, *J. Chem. Soc.*, **105**, 2707 (1914).

(2) R. G. Shulman, *J. Chem. Phys.*, **29**, 945 (1958).

(3) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 299 (1962).

(4) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., 1959, Chapter 10.