inductive effect is obscured by concurrent conjugative effects.

(7) National Science Foundation Predoctoral Fellow, 1960–1963; Eastman Kodak Science Award in Chemistry, 1962–1963.

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Tritiodeprotonation of Biphenylene[1]

Sir:

Because of its unique structure, biphenylene has been of considerable chemical and theoretical interest for some years.[2] The molecular orbital prediction[3] 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 trifluoracetic acid–70% perchloric acid (96.9:3.1 by volume), is similar to that used by Eaborn and Taylor[5] 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-

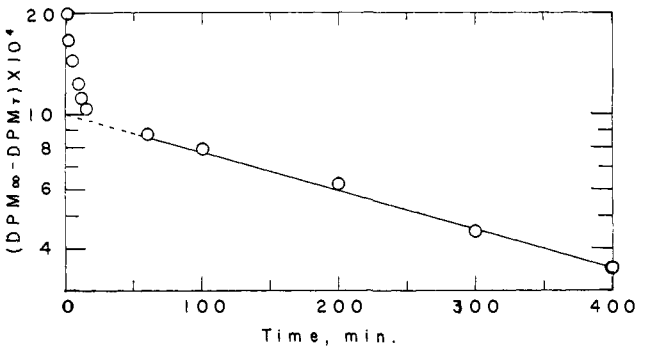

Fig. 1.—Kinetic run for tritiodeprotonation of biphenylene at 25°.

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).

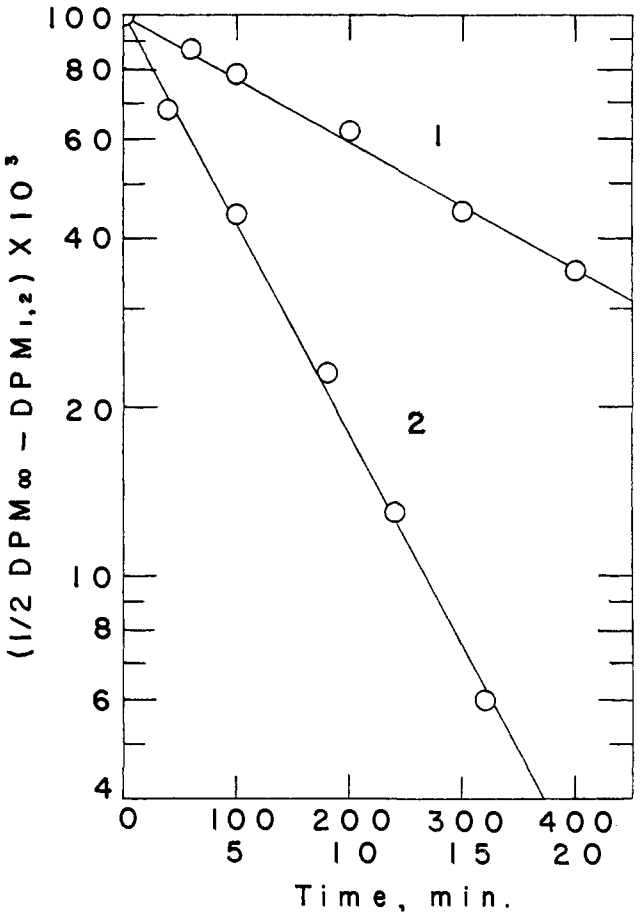

Fig. 2.—Analysis of kinetic run into simultaneous first-order reactions for the 1- and 2-positions of biphenylene. The bottom time scale is for the 2-position.

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 Taylor[5] ($k_\alpha = 5.3 \times 10^{-4}$ 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 $k_\beta/k_\alpha \simeq 4$.[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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N^{14} and C^{13} Nuclear Magnetic Resonance Studies of Iron Hexacyanides

Sir:

This communication reports some results obtained in a C^{13} and N^{14} 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