

Rates of Exchange of Aryl Hydrogens with Lithium Cyclohexylamide in Cyclohexylamine¹

Sir:

In the course of our studies of the acidity of hydrocarbons, we have investigated the rates of hydrogen isotope exchange of a number of specifically deuterated and tritiated arenes with lithium cyclohexylamide in cyclohexylamine at 49.9°. The exchange rates are first order in hydrocarbon and demonstrate the same dependence on lithium cyclohexylamide concentration as does the exchange of toluene- α - d_1 in the same system.² By analogy with this previous work, one would expect the aryl hydrogen exchange to proceed *via* the aryllithium intermediate. Confirming evidence is found in the relatively large decelerating effect of a methyl substituent and accelerating effect of a phenyl

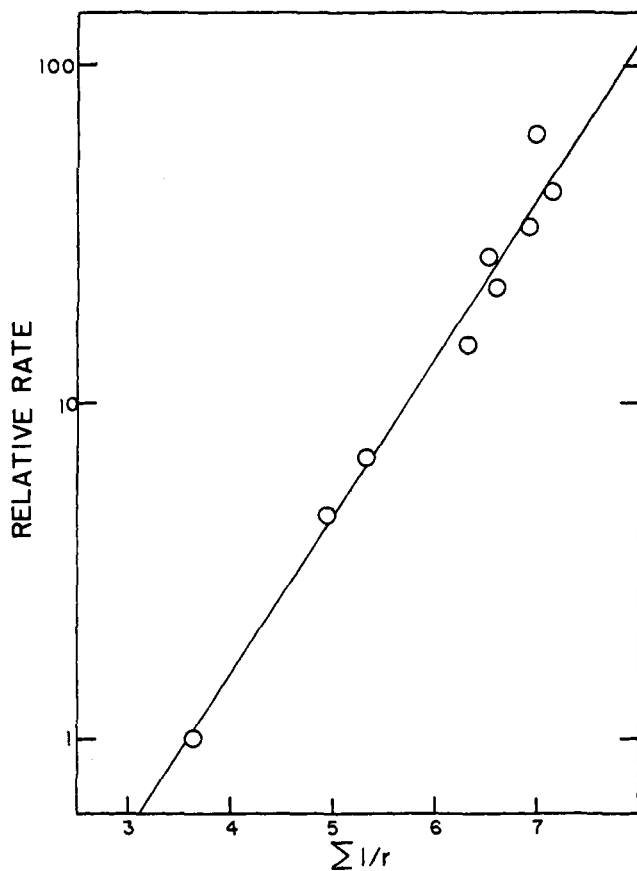


Fig. 1.—Correlation of aryl tritium exchange rates in cyclohexylamine with inverse of distances from sp^2 -hybridized carbon atoms.

substituent on the rate of exchange of the hydrogens of benzene (Table I); these effects are in good agreement with the results of Shatenshtein for the related KNH_2 - NH_3 system.³ Furthermore, a mechanism involving addition of amide to the aromatic ring, followed by protonation and subsequent elimination of amine, is deemed unlikely by our observation of $k_D/k_T = 1.4$, corresponding to $k_H/k_D \approx 2.1$.⁴ For a mechanism involving a rate-controlled addition of amide, one would expect only a small secondary isotope effect.⁵

(1) Acidity of Hydrocarbons. IX. This research was supported in part by grants from the Petroleum Research Fund and by the United States Air Force Office of Scientific Research and Development of the Air Research and Development Command.

(2) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

(3) A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

(4) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).

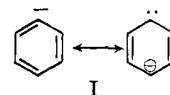
TABLE I
RATES OF EXCHANGE OF R-D AND R-T WITH CYCLOHEXYLAMINE AT 49.9°

R	$k_2^D \times 10^6$, l./mole- sec.	$k_2^T \times 10^6$, l./mole- sec.	$\sum \frac{1}{r}$ ($1/r_{\text{benzene}}$)
Phenyl	3.9	2.3	3.655
3-Tolyl	...	1.24	...
4-Tolyl	...	1.15	...
3-Biphenyl	14.4
4-Biphenyl	8.6
1-Naphthyl	22.2 ^a	...	5.321
2-Naphthyl	14.7 ^a	...	4.932
9-Phenanthryl	70 ^a	...	6.599
9-Anthracyl	179	143	6.988
1-Anthracyl	...	34	6.308
1-Pyrenyl	97	75	6.918
2-Pyrenyl	...	61	6.513
4-Pyrenyl	...	97	7.165

^a For Fig. 1, $k_D/k_T = 1.4$ is assumed.

The exchange rates determined in this study are summarized in Table I. Several conclusions follow from the assumption that these exchange rates are valid measures of the relative stabilities of the corresponding aryl anions.

First, the greater exchange rate of the 3-biphenyl position over the 4-position indicates that carbene-carbanion resonance I is not important in these cases. Second, the perturbation of the π -electron system due to a change in Coulomb integral by the presence of a



negative charge on carbon would also appear to be of minor importance. In such a case, the change in energy may be expressed as⁶

$$\delta E = q \cdot \delta \alpha_r + \frac{1}{2} \pi_{r,r} (\delta \alpha_r)^2 + \dots$$

Since the first term is a constant for alternant hydrocarbons, a correlation between $\pi_{r,r}$ and rate constant would be expected if this π -energy factor were of dominating importance; however, the $\pi_{r,r}$ values⁶ predict several completely wrong orders of reactivity; for example, on this basis, the 2-position of pyrene should exchange more slowly than benzene.

We have found that the experimental results are interpretable quantitatively in terms of a simple electrostatic model in which the carbon bearing the negative charge interacts with each of the π -carbon atoms in the molecule to give a lowering of potential energy proportional to $\sum_i 1/r_i$ in which r_i is the distance from carbon atom i to the carbon bearing the negative charge. Calculations of $\sum_i 1/r_i$ were made for the positions of planar arenes assuming all carbon-carbon bond lengths to be equal to those in benzene. A plot of $\sum_i 1/r_i$ vs. $\log k_T$ is shown in Fig. 1.

We conclude that, despite its general neglect in theoretical studies, this electron-attracting field effect of aromatic π -carbons is an effect of important magnitude in the chemistry of polycyclic, aromatic compounds. In most other reactions of aromatic compounds, this

(5) Our isolation of an addition product of amide to fluoranthene in this system indicates, however, that such a mechanism may occur with the more reactive aromatics. Addition seems to be accompanied by concomitant formation of radical anions. Of the hydrocarbons in this study, only anthracene produces radical anions, but at a rate less than one-tenth that of proton exchange.

(6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 112. The self-atom polarizability, $\pi_{r,r}$, and other symbols are defined in this book.

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-

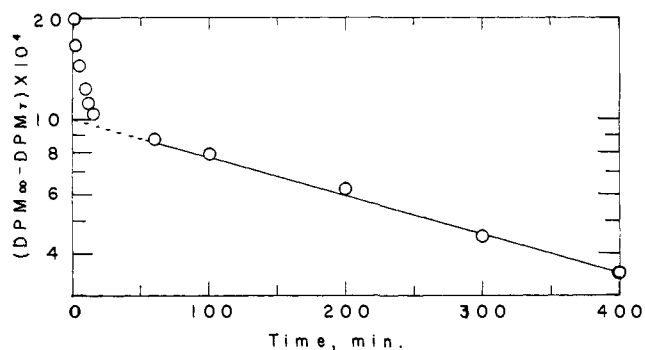


Fig. 1.—Kinetic run for tritiodeprotonation of biphenylene at 25°.

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);

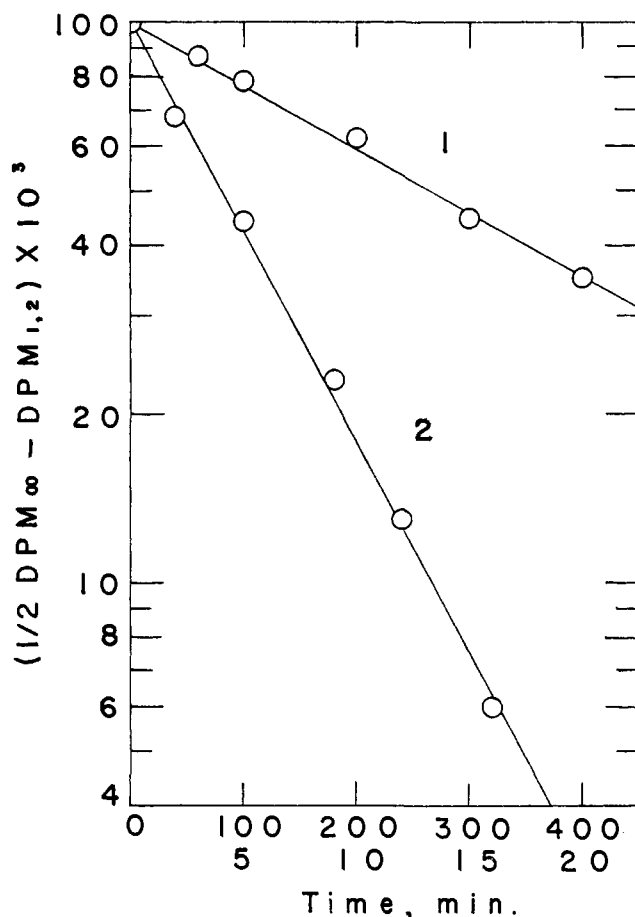


Fig. 2.—Analysis of kinetic run into simultaneous first-order reactions for the 1- and 2-positions of biphenylene. The bottom time scale is for the 2-position.

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