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RATES OF EXCHANGE OF SUBSTITUTED PHOSPHONIUM SALTS

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In a classical piece of research, Doering and Hoffmann (1) reported on the contribution of d-orbital resonance to the rate of deuterium exchange of methyl "onium" salts. Related to that study are the recent investigations of Bestmann (2) who qualitatively pointed out the influence of substituents on the acidity of the methylene group adjacent to quaternary phosphorus. It is in this regard that we wish to report the dramatic rate enhancement (exchange of hydrogen by deuterium) produced by successive replacement of the methyl groups by phenyl substituents in a series of phosphonium salts. The results of this research are given in Table I.

A plot (figure 1) of these data (first four compounds in Table I) is revealing: a consistent rate increase of about twentyfold is achieved by the introduction of each phenyl group. There are a few reported examples in which the additivity of polar effects is apparent (3) and this study can be numbered among them. (4)

The observed rate enhancement provides a measure of the ability of positively charged phosphorus to transmit inductive effects. In order to evaluate the influence of a substituent directly attached to the reaction

TABLE I

Rates of Exchange of Phosphonium Salts[a]

Salt	k_2(l. mole^{-1} sec.$^{-1}$) at 25.0°C	Rel. rate[c]
$(CH_3)_4P^+ I^-$[b]	$7.57 \pm .2 \times 10^{-6}$	1
$C_6H_5P(CH_3)_3^+ Br^-$	$1.30 \pm .05 \times 10^{-4}$	23
$(C_6H_5)_2P(CH_3)_2^+ Br^-$	$1.82 \pm .1 \times 10^{-3}$	481
$(C_6H_5)_3PCH_3^+ Br^-$	$1.82 \pm .07 \times 10^{-2}$	9640
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$(C_6H_5)_3PC_2H_5^+ Br^-$	$1.69 \pm .16 \times 10^{-4}$	134

[a] Determined using the method and conditions described in ref. 1; however, n.m.r. spectroscopy was used to find the percentage of deuterium incorporation.

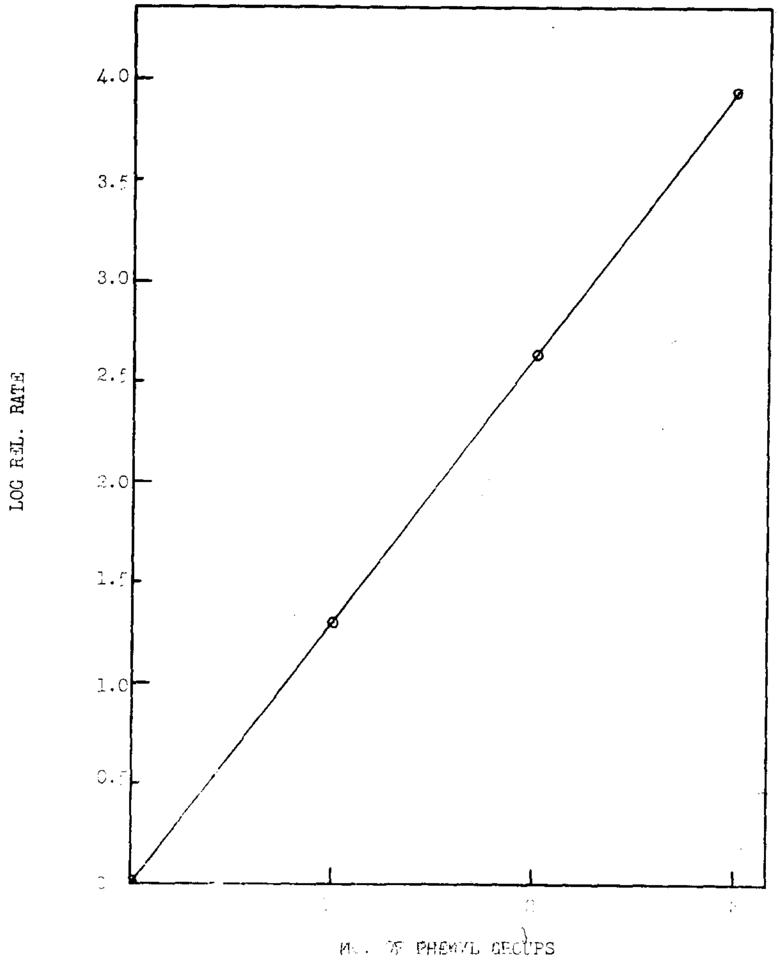
[b] Value calculated from the data in ref. 1.

[c] Statistically corrected for the number of hydrogens available for exchange.

site, the rate for triphenylethylphosphonium bromide was determined. In terms of figure 1, the rate of exchange of the ethyl derivative is equivalent to the hypothetical compound $(C_6H_5)_{1.6}P(CH_3)_{2.4}^+ Br^-$. The rate deceleration (seventyfold compared to the methyl analogue) due to the electron-donating methyl group is indicative of the polar nature of the transition

FIGURE I

Log of the relative rate of exchange versus the number of phenyl substituents. $\Sigma \sigma^*$, the sum of the polar substituent constants σ^* (see ref. 3) at the reaction center ($\gtrdot P-CH_3^+X^-$) parallels the number of phenyl groups and would also give a linear plot.



state. The $(C_6H_5)_3\overset{+}{P}\overset{-}{C}H_2$ / $(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_3$ ratio of 17 obtained by Seyferth (5) from transylidation equilibrium studies is consistent with this view.

Additional work in this and other heteroatomic systems (arsonium and sulfonium salts) are in progress.

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2. H. J. Bestmann, Angew. Chem. Intern. Ed. Engl., 4, 583 (1965), and references therein.

3. For a discussion of the additive nature of polar effects see R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. Newman (ed.), John Wiley and Sons, N. Y. 1956, pp. 623-625.

4. However, the linearity of the present case is in interesting contrast to the relative rates of exchange of the series: toluene, diphenylmethane, and triphenylmethane (1: 270: 1100) determined by A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, J. Am. Chem. Soc., 86, 3578 (1964). A detailed comparison of these systems will be attempted in a future paper.

5. D. Seyferth and G. Singh, J. Am. Chem. Soc., 87, 4156 (1965); D. Seyferth, W. B. Hughes, and J. K. Heeren, ibid., 87, 2847 (1965).