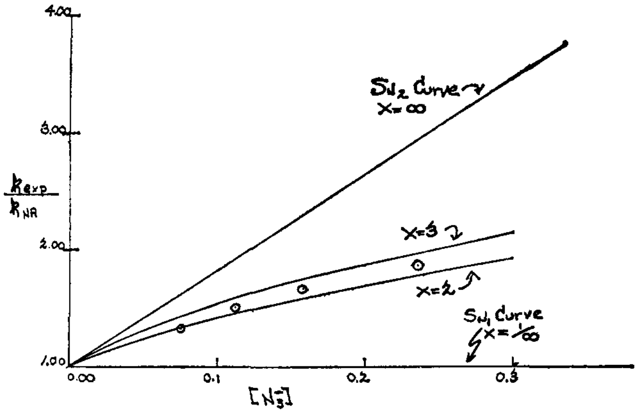

Figure 1. Plot of $k_{\text{exptl}}/k_{\text{NA}}$ *vs.* $[N_3^-]$ for the reaction of 2-octyl mesylate with sodium azide and water in 25 vol. % aqueous dioxane. The solid lines are theoretical plots from eq 3 with $k_N/k_S = 8.22$ and varying values of $x = k_{-1}/k_s$. The experimental points are encircled.

experimental data (k_{exptl}) are well correlated by the ion-pair mechanism (k_{ip}) but deviate considerably, especially at higher salt concentrations, from the rate constants calculated for a true SN2 process (k_{SN2}).

Table I. Kinetics of Solvolyses of 2-Octyl Mesylate in 30 Vol. % Aqueous Dioxane at 36.2°

$[NaN_3]$	% RN_3, exptl	% RN_3,[a] calcd	k_{exptl}, sec^{-1} $\times 10^4$	k_{SN2},[b] sec^{-1} $\times 10^4$, calcd	k_{ip},[c] sec^{-1} $\times 10^4$, calcd
...	...	...	1.74 ± 0.04	...	...
0.0543	38.4	32.3	2.43 ± 0.08	2.74	2.41
0.0571	39.3	34.1	2.26 ± 0.11	2.80	2.43
0.0979	52.5	47.0	2.67 ± 0.14	3.61	2.90
0.152	54.5	57.8	3.65 ± 0.14	4.84	3.50
0.199	64.0	64.3	3.78 ± 0.12	5.88	3.92
0.258	69.3	70.0	4.71 ± 0.08	7.36	4.47
0.311	74.6	73.8	4.91 ± 0.15	8.77	4.92

[a] Calculated from the equation $[RN_3]/[ROH] = 9.04[N_3^-]$. [b] Rate constant calculated from eq 4 assuming an SN2 mechanism with $k_N'/k_s' = 9.04$ and $k_{NA} = 1.74 \times 10^{-4}(1 + 1.04[N_3^-])$. [c] Rate constant calculated from eq 3 assuming an ion-pair mechanism with $k_N/k_s = 9.04$, $x = k_{-1}/k_s = 2.59$, and $k_{NA} = 1.74 \times 10^{-4}(1 + 1.04[N_3^-])$.

Table II. Kinetics of Solvolyses of 2-Octyl Mesylate in 25 Vol. % Aqueous Dioxane at 36.2°

$[NaN_3]$	% RN_3, exptl	% RN_3,[a] calcd	k_{exptl}, sec^{-1} $\times 10^4$	k_{SN2},[b] sec^{-1} $\times 10^4$, calcd	k_{ip},[c] sec^{-1} $\times 10^4$, calcd
...	...	...	2.21 ± 0.08	...	...
0.0758	36.6	38.3	3.18 ± 0.12	3.98	3.28
0.113	44.0	48.1	3.76 ± 0.07	4.80	3.74
0.156	52.2	57.7	4.34 ± 0.17	5.90	4.23
0.237	67.1	66.1	5.18 ± 0.22	8.21	5.17

[a] Calculated from the equation $[RN_3]/[ROH] = 8.22[N_3^-]$. [b] Rate constant calculated from eq 4 assuming an SN2 mechanism with $k_N'/k_s' = 8.22$ and $k_{NA} = 2.21 \times 10^{-4}(1 + 1.08[N_3^-])$. [c] Rate constant calculated from eq 3 assuming an ion-pair mechanism with $k_N/k_s = 8.22$, $x = k_{-1}/k_s = 2.33$, and $k_{NA} = 2.21 \times 10^{-4}(1 + 1.08[N_3^-])$.

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(6) National Institutes of Health Predoctoral Fellow, 1965-1966.

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A New Linear Free Energy Relationship and Its Use as a Diagnostic for Ion-Pair Intermediates[1]

Sir:

That a qualitative relationship exists between the stability of a carbonium ion and its selectivity, as measured by the relative rates of its attack by anions and by solvent, has long been appreciated.[2] That this relationship can be expressed quantitatively is herein reported. More significantly, deviations from this correlation are shown to serve as useful diagnostics for the intermediacy of ion pairs.

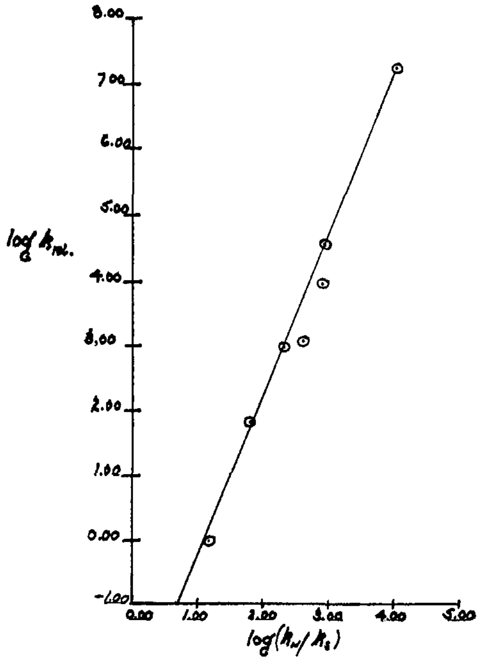
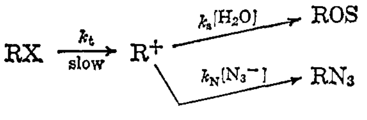


Figure 1. Plot of the logarithm of the relative rates of solvolysis of a series of alkyl chlorides in 80% aqueous acetone at 0° (log k_t) *vs.* the logarithm of the ratio of rates of attack on the corresponding carbonium ions by azide ion and water (log k_N/k_S).

In Table I are assembled rate and selectivity data for a number of alkyl halides and esters known to react *via* carbonium ion intermediates. The nucleophile in all cases is azide ion. The solvolysis rate constant (k_t) and the selectivity ratio (k_N/k_s)[3] are those defined by the scheme



The data have been collected from a number of sources[4]

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(1) Supported in part by the National Science Foundation.

(2) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Am. Chem. Soc.*, **75**, 136 (1953).

(3) This ratio is defined so as to exclude solvent concentration; *i.e.*, $d[ROS]/dt = k_s[H_2O][R^+]$.

(4) An equation originally derived by Swain[2] for the determination of the ratio k_N/k_s is incorrect in that it neglects the consumption of azide ion by liberated strong acid.[5]

$$N_3^- + HX \longrightarrow HN_3 + X^-$$

When this is taken into account the following equation results, which, although it cannot be solved in closed terms, can be solved by successive approximations.

$$\frac{k_N}{k_s} = \frac{[H_2O]}{[ROH]_\infty} \ln \frac{[H_2O] + k_N[N_3^-]_0/k_s}{[H_2O] + k_N\{[N_3^-]_0 - [RX]_0\}/k_s}$$

and are corrected to constant temperature, solvent, and leaving group by standard techniques.

The existence of a linear free energy relationship between the reactivity and selectivity of this group of compounds is established by a plot of log k_t *vs.* log k_N/k_s and results in the rather extraordinarily good correlation line of Figure 1 with slope = 2.83 and intercept = −2.60. Note that compounds which vary in rate by over seven powers of ten are included in this correlation.

Table I. Rates and Selectivities of Alkyl Chlorides on Solvolysis in 80% Aqueous Acetone at 0° in the Presence of Sodium Azide

RCl	k_t, rel.	k_N/k_s
$(CH_3)_3CCl^a$	1.00	1.45×10^1
$(Ph)_2CHCl^b$	6.50×10^1	6.10×10^1
$PhCClHCH{=}CHCH_3{}^c$	9.40×10^2	2.10×10^2
$(CH_3)_2CClCH{=}CH_2{}^d$	1.17×10^3	3.90×10^2
$(p\text{-}MePh)CClHCH{=}CHCH_3{}^c$	9.40×10^3	8.15×10^2
$(p\text{-}MePh)_2CHCl^e$	3.72×10^4	8.70×10^2
$(Ph)_3CCl^f$	1.95×10^7	1.12×10^4

[a] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 960 (1940). [b] M. G. Church, E. D. Hughes, and C. K. Ingold, *ibid.*, 969 (1940). [c] Original data for the *p*-nitrobenzoate ester: R. A. Sneen and A. M. Rosenberg, *J. Am. Chem. Soc.*, **83**, 900 (1961). [d] Unpublished work, P. S. Kay. [e] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940); L. C. Bateman, E. D. Hughes, and C. K. Ingold, *ibid.*, 974 (1940). [f] E. A. Hill, *Chem. Ind.* (London), 1696 (1965).

More significant perhaps than the correlation itself are deviations from it. Thus attempts to correlate the reactivity and selectivity of 2-octyl derivatives with those of Table I are unsuccessful; in fact the experimentally observed selectivity of 2-octyl mesylate[6,7] is *ca.* 3.1 powers of ten, 1250 times greater than predicted by the correlation. Similarly α-methylallyl chloride,[8] with k_N/k_s = 6130, deviates from the correlation by 3.49 log units, or is 3100 times more selective than predicted.

The rationale is both exciting and useful. The compounds of Table I share the common characteristic that the species attacked competitively by solvent and azide ion is almost certainly a dissociated carbonium ion while it has been established[7] that, at least in the case of 2-octyl mesylate, the species attacked competitively is an undissociated ion pair. It would thus seem that nonadherence to the relationship of Figure 1 can serve as a diagnostic for reaction at an ion-pair stage.

Several of the disturbing features of the chemistry of simple allyl chlorides, including the product spreads observed on solvolysis[9] as well as the unusual solvent dependence noted for the bimolecular reaction of allyl chloride with hydroxide ion by Vernon[10] (reaction faster in better ionizing solvents), would now seem to have simple and logical explanations in terms of ion-pair intermediates.[11]

It should be pointed out that the ratio calculated from this revised equation never deviates by more than a factor of two from the original equation which in practice was used to obtain first approximations.

[5] This has been recognized by E. A. Hill, *Chem. Ind.* (London), 1696 (1965).

[6] H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87**, 292 (1965).

[7] R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966).

[8] Unpublished work.

[9] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 794 (1956).

[10] C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

[11] Perhaps it should be noted that this behavior is also observed for the reaction of 2-octyl mesylate with azide ion which is also faster in better ionizing solvents.[6,7] It becomes intelligible when it is recognized that the reaction is in fact a preequilibrium generation of ion pair (favored by better ionizing solvents) followed by attack by azide ion to produce product (disfavored by better ionizing solvents but apparently disfavored to a lesser extent than is the preequilibrium favored).

[12] Fellow of the Purdue Research Foundation, 1964–1965.

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Free Radicals Involving Phosphorus

Sir:

It has been known for several years that arylphosphines and phosphine oxides give colored solutions when treated with alkali metals in polar solvents.[1] However, very few esr studies have been made on these interesting systems.[2-5] Since conflicting results were reported[3,4] for the alkali metal reduction of triphenylphosphine, we have reinvestigated the corresponding reduction of triphenylphosphine oxide. We also wish to report on the effect of replacing the phenyl groups of $(C_6H_5)_3P(O)$ with other groups, and to describe a novel anion radical involving two phosphorus atoms.

The nature of the free-radical species derived from $(C_6H_5)_3P(O)$ depends on the alkali metal and the solvent. Like Hoffmann and Tesch[2] we were able to detect only the biphenyl anion radical (*via* phenyl–P cleavage) in the sodium reduction of $(C_6H_5)_3P(O)$ in 1,2-dimethoxyethane (DME). We obtained the same result with sodium reduction in tetrahydrofuran (THF). However, reduction of $(C_6H_5)_3P(O)$ with potassium in THF at −10° resulted in a blue solution with a 28-line esr spectrum. By contrast, potassium reduction in DME resulted in a red-brown solution with a 10-line spectrum. The 28-line spectrum can be assigned to two sets of overlapping dectets (a 5.25-gauss doublet splitting by P^{31} and a 1.75-gauss dectet splitting from nine equivalent protons in three phenyl groups), each line of which is split into an overlapping set of four lines due to a 0.875-gauss potassium splitting.[6] This evidence suggests that the species in THF solution is $(C_6H_5)_3P(O)\cdot^-$. The 10-line spectrum has a very similar appearance to that reported for $(C_6H_5)_2P\cdot^-$ by Britt and Kaiser.[4] It consists of two sets of overlapping septets with a phosphorus splitting of 7.7 gauss and a 2.6-gauss splitting from six equivalent protons. Under high resolution an additional four-line splitting

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[1] See, for example, F. Hein, H. Plust, and H. Pohleman, *Z. Anorg. Allgem. Chem.*, **272**, 25 (1953); F. Hein and H. Hecker, *Z. Naturforsch.*, **11b**, 677 (1956); and D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958).

[2] A. K. Hoffmann and A. G. Tesch, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

[3] M. W. Hanna, *J. Chem. Phys.*, **37**, 685 (1962); M. I. Kabachnik, V. V. Voevodskii, T. A. Mastryukova, S. P. Solodovnikov, and T. A. Malenteva, *Zh. Obshch. Khim.*, **34**, 3234 (1964).

[4] A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965).

[5] A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, **31**, 112 (1966).

[6] The assignments were aided by calculating spin densities by the Hückel molecular orbital method (Table I). These calculations indicate that the spin densities are very small in the *meta* positions of phosphorus-substituted benzene rings, and, furthermore, that the spin densities of the *ortho* and *para* positions are approximately equal. However, unequivocal assignment must await deuteration experiments.