$$[(C_6H_5)_4P]Br + CH_3Li \longrightarrow (C_6H_5)_4PCH_3 + LiBr$$

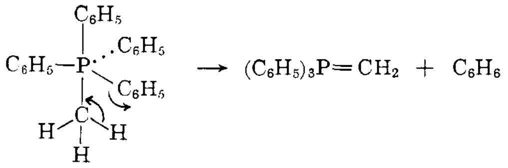
$$(C_6H_5)_4PCH_3 \longrightarrow (C_6H_5)_3P{=}CH_2 + C_6H_6$$

or, (2) an exchange reaction giving the methyltriphenylphosphonium ion, followed by α hydrogen abstraction from the latter

$$[(C_6H_5)_4P]^+ + CH_3Li \longrightarrow [(C_6H_5)_3PCH_3]^+ + C_6H_5Li$$

$$[(C_6H_5)_3PCH_3]^+ + RLi \longrightarrow (C_6H_5)_3P{=}CH_2 + RH + Li^+$$

Wittig and Rieber[5] have demonstrated the easy formation of pentaphenylphosphorane by the reaction of tetraphenylphosphonium bromide with phenyllithium in ether. Thus it seems likely that any organolithium reagent should react with this phosphonium ion in this manner, although the P^V product need not be stable in all cases. Furthermore, the removal of a phenyl anion from pentaphenylphosphorane is relatively easily accomplished, as demonstrated by its reaction with triphenylborane to give tetraphenylphosphonium tetraphenylboron,[6] as well as by other reactions.[2,5] A concerted loss of benzene from a trigonal bipyramidal methyltetraphenylphosphorane intermediate by a cyclic mechanism thus seems easily possible. An attempt to demonstrate the intermediacy of phenyllithium in the methyltriphenylphosphonium bromide–methyllithium reaction gave a negative result. When this reaction mixture was quenched with trimethylchlorosilane immediately after mixing, not even trace amounts of trimethylphenylsilane could be detected.



Indirect evidence favoring a pentacovalent intermediate in the tetraphenylphosphonium bromide–alkyllithium reaction was obtained by a consideration of relative reactivities. Since the experimental procedure used involved adding all of the lithium reagent at one time to the phosphonium salt, the results observed (*i.e.*, quantitative formation of benzene) could only have been obtained *via* the exchange mechanism if the phenyllithium formed were extremely highly favored over methyllithium in the reaction with methyltriphenylphosphonium bromide. If this were not the case, and if the exchange mechanism were operative, then much lower yields of benzene would be expected. Since methyllithium is among the less reactive organolithium reagents,[7] the much more reactive ethyllithium was allowed to react with tetraphenylphosphonium bromide in the same manner. Again, benzene was obtained in nearly quantitative (92%) yield, and ethylidenecyclohexane in 67% yield. Since it is unlikely that the phenyllithium formed in an exchange reaction could complete this successfully with the initially large excess of ethyllithium, the exchange mechanism lacks support, and most likely a pentacovalent ethyltetraphenylphosphorane intermediate is involved.

It should be pointed out that the other extreme in behavior, attack only at the α hydrogen atom of an alkyltriphenylphosphonium salt, is possible. Thus the reaction of methyllithium with benzyltriphenylphosphonium bromide, giving triphenylphosphinebenzylidene, resulted in not even a trace of benzene. Experiments designed to relate the relative importance of the two possible mechanisms to structural factors in the phosphonium salt and the organolithium reagent are in progress.

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DEPARTMENT OF CHEMISTRY DIETMAR SEYFERTH
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS JAMES K. HEEREN
WILLIAM B. HUGHES, JR.

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LARGE SECONDARY INTERMOLECULAR KINETIC ISOTOPE EFFECTS IN NON-EQUILIBRIUM SYSTEMS. ENERGIZATION BY PHOTOSENSITIZATION

Sir:

The occurrence of very large *normal* secondary intermolecular kinetic isotope effects in non-thermally activated unimolecular systems has been described.[1] So far, illustration of this general effect has been given only for systems in which the non-equilibrium distributions of energized molecules has been realized by chemical activation.[1,2] In principle, other experimental techniques such as electron impact, radiation, *etc.*, may be used. We wish to point out the occurrence of the phenomenon for an energization technique other than chemical activation.

In some interesting work by Callear and Cvetanovic[3] collisions of the second kind, $Hg(^3P_1)$ photosensitization at 25°, were used to excite ground state (*N*) ethylene molecules which underwent unimolecular decomposition to split off hydrogen molecules

$$C_2H_4(N) + Hg(^3P_1) \longrightarrow C_2H_4(T) + Hg(^1S_0)$$

$$C_2H_4(T) \longrightarrow H_2 + C_2H_2 \qquad (d_0)$$

Similarly

$$C_2D_4(T) \longrightarrow D_2 + C_2D_2 \qquad (d_4)$$

The nature of the excitation process and decomposition reaction as presented in these equations was described by earlier workers.[4] The excited ethylene species is believed to be both vibrationally and electronically excited to the lowest triplet state (T) of ethylene. The low experimental temperature, together with the operation of the Franck–Condon principle, ensures that the internal energy distribution is highly peaked, *i.e.*, that the excited species are, relatively, vibrationally monoenergetic. Decomposition (if it arises from the excited T state)

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[1] B. S. Rabinovitch and J. H. Current, *Can. J. Chem.*, **40**, 557 (1962).

[2] J. W. Simons, D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 1758 (1962).

[3] A. B. Callear and R. J. Cvetanovic, *J. Chem. Phys.*, **24**, 873 (1956).

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should proceed with conservation of spin angular momentum to give triplet state acetylene.[4]

For the mercury photosensitization of C_2H_4 and C_2D_4, under conditions of complete quenching of the incident radiation, Callear and Cvetanovic estimated the limiting high pressure (30–40 cm.) rate ratio for $H_2:D_2$ production at 4:1. This limiting value is appropriate here since only the relative amounts of decomposition (D) of the excited molecules are recorded. If the amounts of collisional stabilization (S) of excited molecules were also known then the average experimental rate of reaction $k_a = \omega(D/S)$ (where ω = specific collision rate), as defined and used by us previously,[5a] could be calculated for each molecule from data at any pressure.[5b] Failing a knowledge of S, relative rate values are given by the rate measurements for both isotopic systems at (the same) sufficiently high pressure so that $S \simeq 100\%$, *i.e.*, S is virtually the same constant in both cases. This general stipulation should be kept in mind for all rate comparisons of this type,[6] if S is not determined.

The total rate ratio $(k_{ad_0}/k_{ad_4})_\infty$ of $\sim$4:1 is evidently not a "pure" secondary isotope effect since in one case C–H rupture, and in the other C–D rupture, occurs. However, the relative rates of production of H_2 and D_2 by $Hg(^3P_1)$ photosensitization of *cis*-$C_2H_2D_2$, under the same conditions,

$$\begin{aligned} sym\text{-}C_2H_2D_2(T) &\longrightarrow H_2 + C_2D_2 \qquad (d_2) \\ &\longrightarrow D_2 + C_2H_2 \qquad (d_2{}') \end{aligned}$$

is also known. Callear and Cvetanovic give $H_2:D_2$ = 2:1 at 1 cm. pressure. Ausloos and Gorden[6] find the same ratio for both *cis*- and *trans*-$C_2H_2D_2$, independent of pressure over the range investigated, 3–25 cm. We have found an average of 1.9 for this ratio over the pressure range to 16 cm. This intramolecular primary isotope effect (which in one interpretation[3] is given simply by an appropriate mass factor) provides in practise, if not exactly in principle, an adequate calibration of the intermolecular primary isotope correction. The desired secondary effect is then $(k_{ad_0}/k_{ad_4})_\infty \simeq 2$. We have repeated this comparison and our data yield the value $\simeq$1.9, in reasonable agreement. The ratio is quite sizable, even though it refers to replacement of four H atoms.

We have also performed $Hg(^3P_1)$ photosensitization experiments which while simpler in principle are a little complicated in practise: The intermolecular primary isotope correction is eliminated by comparison of H_2 split off for the pair of reactions, (d_0) and (d_2), after allowance for reaction path degeneracy.[6] In practise, since HD and D_2 split from $C_2H_2D_2$ also occur, correction for these processes must be made; the relative split off rates from *sym*-$C_2H_2D_2$ have been given[3,6] as H_2:HD:D_2 = 2:6:1; we have found 2:6:1.05. Also, the reaction pair, (d'_2) and (d_4), similar to the above pair but involving D_2 split off, may be used. By comparison under the same conditions of the rates of split off by C_2H_4, $C_2H_2D_2$ and C_2D_4, experimental errors in the determination of the central $C_2H_2D_2$ decomposition rates are largely eliminated when the (corrected) values of the rate ratio for H_2 split off from the first pair, and for D_2 split off from the second pair, are averaged. The experimental data yield 1.39 as the average value for the ratios $(k_{ad_0}/k_{ad_2})_\infty$ and $(k'_{ad_2}/k_{ad_4})_\infty$. This is an effect resulting from replacement of two H atoms by D.

That the observed ratios are not larger may be plausible from the following considerations. We write for this secondary effect[1]

$$k_{\epsilon H}/k_{\epsilon D} \sim \frac{\sum\limits_{\epsilon^+{}_{vH} \leqslant \epsilon^+{}_H} P(\epsilon^+{}_{vH})}{\sum\limits_{\epsilon^+{}_{vD} \leqslant \epsilon^+{}_D} P(\epsilon^+{}_{vD})} \times \frac{N(\epsilon)_D}{N(\epsilon)_H}$$

where $P(\epsilon_v{}^+)$ is the degeneracy at energy $\epsilon_v{}^+$ of active internal energy states of the activated complex having total active energy ϵ^+; $N(\epsilon)$ is the density of energy levels of the molecule at active energy ϵ.[7] The sum ratio tends to compensate the density ratio. The magnitude of the expression $k_{\epsilon H}/k_{\epsilon D}$ increases in general as $\epsilon \rightarrow \epsilon_0$ (where ϵ_0 is the critical energy), *i.e.*, as $\epsilon^+ \rightarrow 0$, so that the sum ratio tends to unity.

Now the energetics and mechanism of the present system are complicated by the occurrence of electronic state changes; by the fact that the minimum of the triplet[8] surface at a torsion angle near 90° is imprecisely located[9]; and by the *possibility*, among others[3], that decomposition occurs from the vibrationally excited singlet state arising by intersystem crossing, (T) → (N). Thus the appropriate values of ϵ and ϵ^+ are not known. However, it *is* known that although split off occurs readily by $Hg(^3P_1)$ sensitization (112 kcal./mole), it may barely take place, if at all, by $Zn(^3P_1)$ sensitization (93 kcal.).[10] Thus for mercury photosensitization ϵ^+ may have some value up to 19 kcal./mole, and is probably *not* close to zero. The magnitudes found above are thus quite reasonable.

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DIVISION OF APPLIED CHEMISTRY
NATIONAL RESEARCH COUNCIL B. S. RABINOVITCH[11]
OTTAWA, CANADA
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON D. W. SETSER
SEATTLE 5, WASH.

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(6) P. Ausloos and R. Gorden, *J. Chem. Phys.*, **36**, 5 (1962). Experiments with *asym*-$C_2H_2D_2$ showed that a single scramble mechanism, proposed by Callear and Cvetanovic, substantially, if not completely, describes the split off reaction.

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(11) Visiting Scientist; John Simon Guggenheim Memorial Fellow, 1961–62, and Petroleum Research Fund International Award Fellow, 1961–62. N.R.C. Contribution No. 6834.