showing the complex to be diamagnetic.[2] This is anticipated, since the proposed structure contains rhenium in the 1+ state. The lack of a high-field "hydride" resonance indicates the probable absence of a rhenium-bound hydrogen.[3]

The mass spectrum[4] of I gives further support to the above formulation. A parent peak, $(M)^+$ (*m/e* 1130),[5] was observed with a relative intensity of 43.8% compared to the $(M - 5CO)^+$ peak. In addition to several low-intensity and doubly charged peaks, an $(M - 6CO)^+$ peak was also observed (68.9%). Since naturally occurring rhenium has two common isotopes, ^{185}Re and ^{187}Re, the triplet at $(M)^+$, $(M + 2)^+$, and $(M + 4)^+$ further supports the presence of two rhenium atoms in each molecule.

(Monohydrogen mesoporphyrin IX dimethyl esterato)tricarbonylrhenium(I) (II) recrystallized as clumps of brown microcrystals from benzene–hexane. It melted at 190–192° and was distilled under vacuum at 240° onto a cold finger of the sublimation apparatus. *Anal.* Calcd for $ReC_{39}H_{41}N_4O_7$: C, 54.21; H, 4.78; Re, 21.57. Found: C, 54.93; H, 4.89; Re, 22.24. In benzene it gave a brown solution with three broad visible absorptions at 585 nm (ϵ 6.2 × 10^3), 485 (2.0 × 10^4), and 392 (1.1 × 10^5). Its ir spectrum was similar to that of I, having absorptions at 3380 (N–H stretch), 1900, and 2015 cm^{-1}. The proton magnetic resonance (pmr) spectrum of the brown complex was that of a complexed porphyrin with the addition of a broad ($W_{1/2}$ = 6 cps) peak at τ 14.9 corresponding to a single proton. The sharp spectrum is again indicative of a diamagnetic complex. Addition to the $CDCl_3$ solution of a small amount of DCl in D_2O caused the immediate disappearance of this peak. A comparison of the chemical shift of this exchangeable proton with that of the N–H protons in uncomplexed porphyrins (*e.g.*, τ 13.9 for mesoporphyrin)[6] leads us to believe that the proton observed here is similarly bonded to the porphyrin nitrogens. The presence of this proton would also put the rhenium atom in the 1+ state and explain the observed diamagnetism. If the proton was attached to the metal atom, we would expect the pmr absorption to occur at higher field, in the neighborhood of τ 20. By comparison, the Re–H proton of $ReH(C_5H_5)_2$ occurs at τ 23.[7]

The mass spectrum of II showed a parent peak $(M)^+$ (*m/e* 862)[8] with a relative intensity of 8.8% compared to the $(M - 3CO)^+$ peak. There were also several low-intensity and doubly charged peaks. The relative intensities of the doublet at $(M)^+$ and $(M + 2)^+$ support the presence of one rhenium atom per molecule. Further, the ratio of $(M - H)^+$ to $(M)^+$ for II is 4.5 times as large as for I. This seems to confirm, as surmised from pmr studies, the presence of a nitrogen-bonded proton in II and its absence in I.

Compound I can be prepared without significant amounts of II by using excess rhenium carbonyl and long (10 hr) reaction times. Compound II can also be prepared in similar purity by allowing stoichiometric quantities of rhenium carbonyl and porphyrin to react for a period of 1 hr.

One can convert II to I by reaction with rhenium carbonyl as in the preparation of I from porphyrin. However, attempts at the conversion of I to II by reflux in decalin with excess porphyrin were unsuccessful in periods of up to 24 hr.

On the basis of these experiments one can propose the following reaction scheme, where P represents the porphyrin dianion.

$$^1/_2Re_2(CO)_{10} + PH_2 \longrightarrow Re(PH)(CO)_3 \quad (1)$$

$$Re(PH)(CO)_3 + {}^1/_2Re_2(CO)_{10} \longrightarrow (CO)_3RePRe(CO)_3 \quad (2)$$

A single-crystal X-ray diffraction analysis will be needed to determine whether there is a metal–metal bond in I and whether the four porphyrin nitrogens are arranged to form a planar or a "puckered" ring. The latter question is significant in determining the exact arrangement of bonds between metal and porphyrin.

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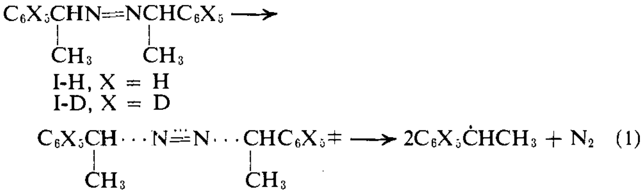
A Classical Mechanical Isotope Effect. The Effect of Ring Deuterium on the Rate of Pyrolysis of 1,1′-Diphenylazoethane

Sir:

The thermal decomposition of 1,1′-diphenylazoethane (I-H) proceeds *via* simultaneous rupture of both carbon–nitrogen bonds[1] (eq 1). We report that the kinetic isotope effect in the decomposition of ring-deuterated I-H (I-D) is nearly, if not completely, classical mechanical[2] ($\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$) in origin. To our knowledge this is the first direct measurement of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ at "low" temperatures.



$$C_6X_5\underset{\displaystyle CH_3}{\underset{|}{C}}HN{=}N\underset{\displaystyle CH_3}{\underset{|}{C}}HC_6X_5 \longrightarrow$$

I-H, X = H
I-D, X = D

$$C_6X_5\underset{\displaystyle CH_3}{\underset{|}{C}}H\cdots N{\equiv}N\cdots\underset{\displaystyle CH_3}{\underset{|}{C}}HC_6X_5{}^{\ddagger} \longrightarrow 2C_6X_5\dot{C}HCH_3 + N_2 \quad (1)$$

Compounds I-H and I-D were synthesized[1c] by catalytic hydrogenation of acetophenone[3] and acetophenone-d_{10}[4] azines in benzene (I-H, mp 71–72°, lit.[1c] mp 71.8–72.7°; ϵ (benzene) 45.8; λ_{max} 360 mμ), *p*-

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dioxane (I-D, sample 1, mp 71.5–72.5°; ϵ (benzene) 45.1; λ_{max} 360 mμ), and benzene (I-D, sample 2, mp 71.2–71.7°; ϵ (benzene) 45.3; λ_{max} 360 mμ). Mass spectrometric analysis[4] (15 and 12.5 eV nominal) of the d_{10} azine yielded 99.50 ± 0.24 atom % D. Using *p*-dioxane as an internal standard, nmr analysis gave 1.97 ± 0.04 and 2.01 ± 0.04 atoms of α-H for samples 1 and 2, respectively. Analysis of the benzoic acid-d_5 obtained from oxidation[1c] of samples 1 and 2 of I-D yielded 99.13 ± 0.45 and 99.40 ± 0.12 atoms of D. As expected,[5] catalytic reduction of the d_{10} azine occurs with essentially no exchange of aromatic deuterium. The isotope effects determined by simultaneously observing the rates of disappearance of I-H and I-D in ethylbenzene[6] are tabulated in Table I.

Table I. Isotope Effect in the Thermal Decomposition of 1,1′-Diphenylazoethane-d_{10} in Ethylbenzene

Compound	Temp, °C	$(k_H/k_D)_{obsd}$[a]
I-H/I-D[b]	104.58 ± 0.06	1.030 ± 0.007[d]
I-H/I-D[c]	104.57 ± 0.05	1.030 ± 0.007[e]

[a] All deviations are standard deviations. [b] Sample 1. [c] Sample 2. [d] Average of seven determinations. [e] Average of five determinations.

Within the limits of experimental precision, the possible presence of *ca.* 0.06 atom of α-D does not alter k_H/k_D, *i.e.*, $(k_H/k_D)_{corr} = (1/1.27)^{0.06/2.0}(1.030) = 1.023$, where 1.27 is the α effect for I.[1c] Furthermore, the agreement in k_H/k_D for samples 1 and 2 is excellent.

The isotope effect can be expressed as the product of the classical mechanical and quantum mechanical (*VP* × *EXC* × *ZPE*) contributions[7] (eq 2). The

$$k_H/k_D = \nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger} \times VP \times EXC \times ZPE \qquad (2)$$

contribution of *VP* × *EXC* × *ZPE* to k_H/k_D was estimated as follows. Observed rates of pyrolysis of 1,1′-(3,3′- and 4,4′-disubstituted)diarylazoethanes (meta and para substituted I-H) are listed in Table II.

Table II. Rates and Relative Rates for Pyrolysis of 1,1′-(3,3′- and 4,4′-Disubstituted)diarylazoethanes in Ethylbenzene at 104.57°

Substituent	$k \times 10^5$, sec^{-1} [a]	Rel rate	σ[f]	σ^+ [f]
H	8.29[b]	1.00	0.00	0.00
m-CH_3	8.29[c]	1.00	−0.069	−0.066
p-CH_3	9.60[d]	1.16	−0.170	−0.310
p-CH_3O	11.5[e]	1.39	−0.268	−0.778

[a] Calculated from data at other temperatures. [b] $k = 2.13 \times 10^{-4}$ and 9.08×10^{-5} sec^{-1} at 112.91 and 105.35°. [c] $k = 2.14 \times 10^{-4}$ and 9.08×10^{-5} sec^{-1} at 112.91 and 105.35°. [d] $k = 2.44 \times 10^{-4}$ and 10.2×10^{-5} sec^{-1} at 112.91 and 105.13°. [e] $k = 2.93 \times 10^{-4}$ and 12.3×10^{-5} sec^{-1} at 112.91 and 105.13°. [f] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 204.

Table III. Ring Deuterium Isotope Effects for Solvolysis of Benzhydryl Chloride and Calculated Quantum Mechanical Effects for I-H/I-D

	II-H/II-D		I-H/-ID, 104.57°	
Position of D	k_H/k_D[a,b]	*VP* × *EXC* × *ZPE*[b]	*VP* × *EXC* × *ZPE* $\rho = -0.095$	*VP* × *EXC* × *ZPE* $\rho = -0.275$
Ortho	0.9823	0.9813	0.9996[c]	0.9990[c]
Meta	0.9862	0.9852	0.9986[c]	0.9960[c]
Para	0.9901	0.9891	0.9995[d]	0.9985[d]
Totals for I-H/I-D			0.998[e]	0.994[e]

[a] Data for 70 and 80% aqueous acetone at 25°. [b] Per atom of D. [c] For four atoms of D. [d] For two atoms of D. [e] For ten atoms of D.

Linear least-squares plots of log (k_X/k_H) as a function of σ^+ and σ yield $\rho_{I\text{-}H}$ values of −0.095 ± 0.007 and −0.275 ± 0.056 at 104.57°, respectively. Isotope effects reported for solvolysis of benzhydryl chloride (II-H) and specifically ring-deuterated benzhydryl chlorides (II-D) are tabulated in Table III.[8] For II-H/II-D the mass fragment approximation[2] yields a value of 1.0010 for $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$. From eq 2 the quantum mechanical contribution to the isotope effect is given by $(k_H/k_D)/(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})$. The values of this quantity for the various II-D's are shown in column 3 of Table III. For each ring position in I-D, the quantum mechanical effect per D was estimated using eq 3.[8,9] The value of $\rho_{II\text{-}H}$ in eq 3 was taken to be −4.03.[10] A

$$\log (VP \times EXC \times ZPE)_{I\text{-}H/I\text{-}D} = (\rho_{I\text{-}H}/\rho_{II\text{-}H}) \log (VP \times EXC \times ZPE)_{II\text{-}H/II\text{-}D} \qquad (3)$$

value of $(VP \times EXC \times ZPE)_{I\text{-}H/I\text{-}D}$ obtained from eq 3 was then raised to the power equal to the number of deuteriums in equivalent positions in II-D (columns 4 and 5, Table III). The magnitude of the quantum mechanical effect for I-H/I-D is thus calculated to be *ca.* 1% for ten atoms of D. The data for II-H (II-D) were obtained at 25°. However, extrapolating the rate constants for I-H to 25° and determining the magnitudes of ρ do not affect, in terms of the precision in k_H/k_D, the calculated values of *VP* × *EXC* × *ZPE* for I-H/I-D, *i.e.*, the values at 25° are 0.997 and 0.990, respectively. Clearly, delocalization of the incipient odd electron in the transition state for I-H results in a negligible perturbation of the aromatic carbon–hydrogen force constants. Assuming the reaction coordinate for I-H (I-D) to be the symmetric stretching frequency,[1d] the fragment model yields a value of 1.024 for $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$, *i.e.*, $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger} = (m_{Y\text{-}D}/m_{Y\text{-}H})^{1/2}$, where $m_{Y\text{-}D}$ and $m_{Y\text{-}H}$ are the masses of $C_6D_5CHCH_3$ and $C_6H_5CHCH_3$, respectively. This value may be regarded as a lower limit to the correct value. For example, for I-methyl-d_6 the "exact" value for $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ (1.026) is larger than the value from the fragment model (1.014).[11] Tentatively and without attempt at justification, an alternative value of 1.044, *i.e.*, $(1.026)^{10/6}$, is assumed for $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for I-H/I-D. The value of k_H/k_D, 1.030, is encompassed by this

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Table IV. Experimental Range of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for I-H/I-D

$-\rho$	k_H/k_D	$VP \times EXC \times ZPE$	$(\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger})_{\text{exptl}}$
0.095	1.037	0.998	1.039
	1.030	0.998	1.032
	1.023	0.998	1.025
0.275	1.037	0.994	1.043
	1.030	0.994	1.036
	1.023	0.994	1.029

range in $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$, 1.024–1.044. Table IV lists experimental values of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for I-H/I-D obtained by combining values of $VP \times EXC \times ZPE$ from Table III with the value of $k_H/k_D \pm \sigma_{k_H/k_D}$. The theoretically calculated and experimentally determined ranges of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ are in good agreement, *i.e.*, 1.024–1.044 and 1.025–1.043, respectively.[12] The observed isotope effect is thus principally if not completely determined by $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$.

The importance of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ results from its being a function of the nature of the transition state.[7,13] Consequently, calculations of "exact"[7] values of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ for various transition states for I-H (I-D) are in progress, with the view of unambiguously defining the nature of the pyrolytic transition state for I-H.

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[12] Use of the $VP \times EXC \times ZPE$ values calculated at 25° yields a range in $(\nu_{1L}{}^{\ddagger}\nu_{2L}{}^{\ddagger})_{\text{exptl}}$, 1.026–1.047, which, within the limits of experimental precision, is equivalent to the ranges in Table IV.

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The Magnitude of Secondary α-Deuterium Isotope Effects for Limiting Solvolyses[1]

Sir:

The tendency of the solvolytic secondary α-deuterium isotope effect[2,3] to increase with decreasing disposition of the substrate toward rearside nucleophilic attack or with decreasing nucleophilicity of the solvent (or attacking group) has been used as a means of assessing the limiting nature of solvolysis.[2–8] While the lower limit of the α-deuterium isotope effect is unity or slightly less for SN2 reactions,[3,4a,j,5] determination of the maximum value for limiting solvolyses has posed difficulties. Not only does the magnitude of α-D isotope effects depend on the degree of nucleophilic involvement, but also on the leaving group[4k] and on ion-pair partitioning effects.[7b] The highest recorded values of the α-deuterium isotope effect for secondary arenesulfonates (k_H/k_D = 1.16–1.23) in saturated systems were determined with substrates sterically susceptible to backside nucleophilic attack (Table I). α-Deuterium isotope effects in this range have often been interpreted as indicating limiting behavior.[9] These conclusions are at variance with other criteria[10] which indicate that the behavior of the substrates listed in Table I is *not* limiting. For example, their *m* values and apparent *m* values are all significantly less than the experimental maximum for a secondary substrate (Table I).[11]

We have recently presented extensive evidence indicating that 2-adamantyl derivatives, unlike simple secondary alkyl derivatives such as 2-propyl or cyclohexyl, solvolyze with little or no nucleophilic solvent participation.[10,12] For this reason we have determined the rates of solvolysis of 2-adamantyl tosylate and 2-adamantyl-*2-d* tosylate in four solvents ranging from trifluoroacetic acid (low nucleophilicity)[8d,13] to 80% ethanol (high nucleophilicity)[14] in the hope of establishing maximum experimental values of the α-deuterium isotope effect for arenesulfonate leaving groups. During the course of reporting this work, two closely related studies from Shiner's laboratory[4k,l] were brought to our attention. Shiner and Dowd showed that the 3-pentyn-2-yl system apparently was limiting and gave as high

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[11] 2-Adamantyl tosylate gives maximum values for secondary substrates: apparent $m = 0.89$, $m = 0.91$.[10a] See ref 10a for a discussion of this use of *m* values. In addition to *m* values, other criteria such as $(k_{\text{EtOH}}/k_{\text{AcOH}})_y$[10a] and per cent inversion[4b] indicate the nonlimiting behavior of the substrates listed in Table I. See also S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).

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