the predominant excimer formed fluoresces at shorter wavelength and decays preferentially to dimer **2**. Since there is little spectroscopic evidence of strong association at any concentration of **1** in either homogeneous solution or reversed micelles, it is likely that the orientation is controlled by interaction of the stilbazolium cations with the negatively charged interface rather than to preferential association of the cations in what would be expected to be a Coulombically unfavorable arrangement. The striking increase in selectivity and quantum efficiency to produce a photoproduct not observed in homogeneous solution indicates a degree of topological control of reactivity in the AOT reversed micelles previously associated chiefly with the crystalline state. We are currently extending our studies to other photoreactive ions to determine whether the ability of these charged interfaces to orient ionic reactants is a general and/or tunable property.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8315303) for support of this research.

Measurement of Rates and Equilibria for Keto–Enol Tautomerism of Aldehydes Using Horseradish Peroxidase Compound I

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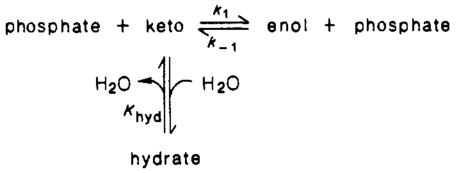
Measurement of the relevant kinetic and thermodynamic parameters for keto–enol tautomerism of aldehydes has presented a major challenge, caused mainly by difficulties in measuring the small concentration of the enol form present in most systems.[2] From investigations of the horseradish peroxidase catalyzed reaction of 2-methylpropanal (isobutyraldehyde) and molecular oxygen to form triplet-state acetone and formic acid, it has been established that only the enol form of the aldehyde is reactive with compounds I and II of peroxidase.[3] We report here upon exploitation of this reactivity of enols to measure the rate and equilibrium constants for the keto–enol tautomerism of 2-methylpropanal, propanal, and butanal.

Compound I (HRP-I) was prepared in close to pure form (with only inert native enzyme present as a small contaminant) and introduced into one reservoir of a stopped-flow apparatus (Union Giken Model RA-601).[4] 2-Methylpropanal, solubilized in up to 0.59 M aqueous ethanol, was placed into the other reservoir. All reactions were studied at 35.0 °C, pH 7.4, and ionic strength 0.67 M. K_2SO_4 was used as an inert electrolyte where necessary. Phosphate buffer was used; it catalyzes the keto–enol conversion. The relevant equations are


(1)

$$\text{phosphate} + \text{keto} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{enol} + \text{phosphate} \quad (1)$$
$$\text{keto} \underset{K_{hyd}}{\overset{H_2O \quad H_2O}{\rightleftharpoons}} \text{hydrate}$$

$$K_{enol} = \frac{[\text{enol}]}{[\text{keto}]} = \frac{k_1}{k_{-1}} \quad (2)$$

$$\begin{aligned}[\text{aldehyde}]_{tot} &= [\text{keto}] + [\text{hydrate}] + [\text{enol}] \\ &\simeq [\text{keto}] + [\text{hydrate}] \end{aligned} \quad (3)$$

$$K_{hyd} = \frac{[\text{hydrate}]}{[\text{keto}]} = \frac{[\text{aldehyde}]_{tot} - [\text{keto}]}{[\text{keto}]} \quad (4)$$

$$\therefore [\text{keto}] = \frac{[\text{aldehyde}]_{tot}}{1 + K_{hyd}} \quad (5)$$

Molecular oxygen does not play any role in the elementary reactions described here, only in the overall reaction.[3]

With enol in excess with respect to compound I a pseudo-first-order reaction is observed at 411 nm, the isosbestic point between native enzyme and compound II,

$$\begin{aligned} -d[\text{HRP-I}]/dt &= k_{obsd}[\text{HRP-I}] \\ &= k_{app}[\text{enol}][\text{HRP-I}] \end{aligned} \quad (6)$$

where the units of k_{obsd} are s^{-1} and of k_{app} are $M^{-1}\ s^{-1}$. From eq 2, 5, and 6,

$$k_{obsd} = k_{app}[\text{enol}] = \frac{k_{app}K_{enol}[\text{aldehyde}]_{tot}}{1 + K_{hyd}} \quad (7)$$

A plot of k_{obsd} vs. total aldehyde concentration is linear with the slope equal to $k_{app}K_{enol}/(1 + K_{hyd})$. Thus if the equilibrium constants are known, the rate constant for the reaction of compound I with enol, k_{app}, can be calculated. This approach was valid for 2-methylpropanal and propanal but not for butanal because of its low solubility. The values of k_{app} are of the order of $5 \times 10^6\ M^{-1}\ s^{-1}$.

More complicated but more revealing behavior is observed when compound I is in excess of enol. Now the consumption of compound I consists of an initial burst in which the equilibrium pool of enol is consumed rapidly, followed by a slow zero-order reaction in which the rate-limiting step is the keto–enol conversion. The steady-state approximation is valid in the zero-order region and it can be shown that

$$-d[\text{HRP-I}]/dt = \frac{k_1[\text{aldehyde}]_{tot}[\text{phosphate}]}{1 + K_{hyd}} = k_{zo} \quad (8)$$

where k_1 is the second-order rate constant for the conversion of keto to enol, catalyzed by phosphate, and k_{zo} is the experimentally determined zero-order rate constant ($M\ s^{-1}$). For fixed $[\text{aldehyde}]_{tot}$ a plot of k_{zo} vs. [Phosphate] is linear; similarly for fixed phosphate a plot of k_{zo} vs. $[\text{aldehyde}]_{tot}$ is linear. Therefore k_1 is calculated readily if K_{hyd} is known. Unfortunately, some measurements of K_{hyd} in the literature are inconsistent or obtained under different experimental conditions.[5] The multiplication factor $(1 + K_{hyd})$ therefore has not been applied to the values reported in Table I. We define new parameters K'_{enol} and k'_1 which are the ones listed in Table I.

$$K'_{enol} = K_{enol}/(1 + K_{hyd}); \quad k'_1 = k_1/(1 + K_{hyd}) \quad (9)$$

The factor $(1 + K_{hyd})$ cancels in the determination of k_{-1}. By calibration of the stopped-flow apparatus, the amount of compound I disappearing in the initial burst can be determined; this provides a measure of the equilibrium concentration of enol and hence of the equilibrium constant K'_{enol}. Since both k'_1 and K'_{enol} have been determined, k_{-1} can be calculated. A similar approach was used for propanal and butanal for which no experimentally determined constants appear in the literature. Results are summarized in

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Table I. Data on Phosphate-Catalyzed Keto–Enol Tautomerism of Aldehydes and Compound I Reactions with Enols at 35 °C[a]

	equilibrium constant [enol]/[keto] K'_{enol}	rate constants, M^{-1} s^{-1} keto + phosphate k'_1	rate constants, M^{-1} s^{-1} enol + phosphate k_{-1}
2-methylpropanal	1.2×10^{-4}	6.0×10^{-5}	0.5
propanal	8.0×10^{-6}	1.5×10^{-4}	19
butanal	5.5×10^{-6}	1.0×10^{-4}	19

[a] Ionic strength 0.67 M and pH 7.4; to correct for hydrate formation, multiply K'_{enol} and k'_1 by the factor $(1 + K_{hyd})$.

Table I. For 2-methylpropanal K_{enol} is 1.7×10^{-4} and k_1 8.6×10^{-5} M^{-1} s^{-1} with a correction for hydrate formation.[6] These results compare favorably with those obtained by other experimental and theoretical methods.[2]

Both propanal and butanal have cis–trans isomers in their enol forms. Our results can be fit with a single exponential curve for the burst phase which is followed by the linear zero-order phase. The burst results indicate either that there is no detectable difference in reactivity of the two geometric isomers with compound I, which would appear likely because of the known lack of selectivity in compound I reactions, or that one isomer is dominant. The observed linear behavior following the burst could be the sum of two zero-order reactions, one for each isomer.

Thus we have described a unique technique using peroxidase compound I for measuring rates and equilibria of keto–enol tautomerism which could readily be applied to a study of the influence of acid–base catalysts upon the rates.

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Phosphinocarbene–Phosphaalkene Rearrangement and Intramolecular Wittig-like Reaction Involving a Phosphorus Vinyl Ylide

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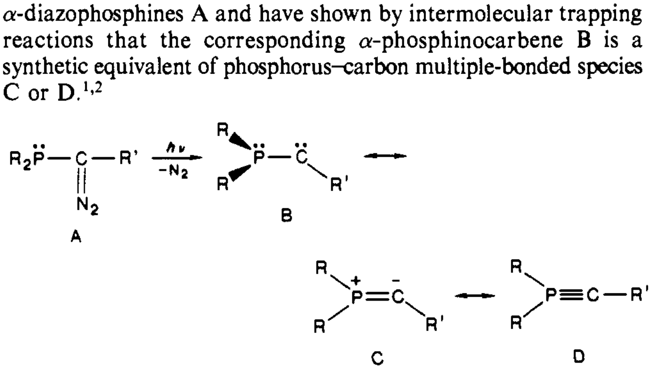
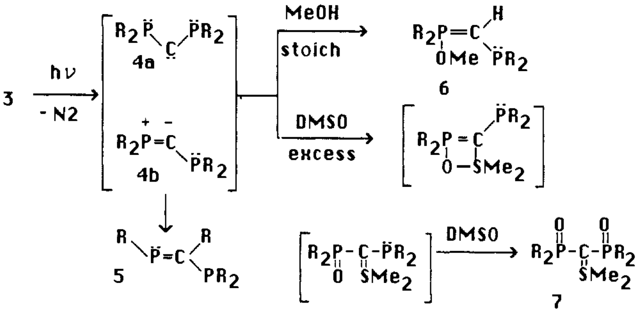
During the last decades, two of the most fascinating areas in chemistry have been the synthesis and reactivity of electron-deficient species and of p_π–p_π multiply bonded heavier main-group-element derivatives. We have recently prepared the first α-diazophosphines A and have shown by intermolecular trapping reactions that the corresponding α-phosphinocarbene B is a synthetic equivalent of phosphorus–carbon multiple-bonded species C or D.[1,2]



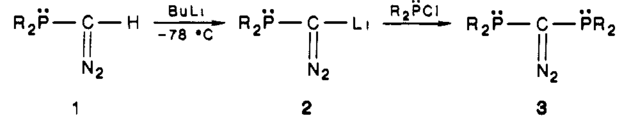
R = (*i*-Pr)$_2$N; R' = SiMe$_3$

Scheme I



Here we wish to report that, although phosphinocarbenes always possess a multiple-bond character, intramolecular rearrangements typical of either carbene or ylide behavior may occur, depending on the nature of the diazo–carbon substituent.

Bis(phosphino)diazomethane 3[3] was prepared by a two-step, one-pot reaction from the [bis(diisopropylamino)phosphine]diazomethane (1)[1] via the corresponding lithium salt 2.



R = (*i*-Pr)$_2$N

From an acetonitrile–benzene solution, 3 recrystallized at room temperature as air-stable orange crystals in 85% yield and was fully characterized including by X-ray analysis.[4] Of particular interest, the N–N bond length (1.15 Å) is slightly longer, and the C–N bond distance (1.28 Å) is slightly shorter, than those observed in diazoalkanes.[5] The lower multiplicity of the nitrogen–nitrogen bond is confirmed by a low IR frequency (2010 cm^{-1}).

Photolysis in benzene solution at 300 nm or attempted distillation of 3 at 100 °C (10^{-2} mmHg) led to phosphaalkene 3[3] in nearly quantitative yield. This rearrangement could either result from a concerted migration–nitrogen-loss mechanism or involve a phosphinocarbene intermediate 4. In fact, products 6 and 7,[3] obtained by irradiation of 3 in the presence of methanol and dimethyl sulfoxide, respectively, clearly demonstrate the intermediacy of a phosphinocarbene 4 possessing phosphorus–carbon multiple-bond character (Scheme I). Note that the trapping agents do not react with 3 in the absence of UV light.

Addition of the lithium salt 2 to acyl chlorides led after workup to a mixture of acetylenic derivatives **10**[3] and 1,3,4-oxadiazoles **9**[3] that were fully characterized, including an X-ray analysis for **9b**.[4] However, when trimethylacetyl chloride was used, phosphino diazo ketone **8a** was observed in solution at 0 °C by NMR (δ ^{31}P +70.6) and IR ($\nu(CN_2)$ 2045, $\nu(CO)$ 1640 cm^{-1}) spectroscopy. Products **10** can also be obtained in one step by heating the silylated diazophosphine **11**[1] with acyl chlorides (Scheme II).

In contrast with 3, no 1-2 shift, which would have led to phosphaalkenes **13** or phosphinoketenes **14**, was observed. It seems quite reasonable to postulate that **10** results from an intramolecular Wittig-like reaction involving a phosphorus vinyl ylide **12b** (Scheme III).

These results, as a whole, support theoretical calculations that predict, for the parent compound H_2PCH, a phosphinocarbene phosphorus vinyl ylide separation of only 4 kcal/mol[6] and a small energy barrier for the rearrangement to the more thermodynamically favored phosphaalkene structure. Moreover, it is clear that although α-dicarbenoid species of the first-row elements always behave as triple-bonded compounds;[7] in contrast, when a second

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