$(CH_3)_2$, ~2.6 (4 H, broad, $-CH_2CH_2-$), 3.85 (1 H, m, CH), and 6.55–8.10 ppm (24 H, m, aromatic).

The opposite sign of rotation found in the phosphine recovered from reaction 1 compared to that from complex **4** or **5** demonstrates that the resolution was effected by a stereospecific reaction of the asymmetric complex **2** with the tertiary phosphines. Resolutions of some cyclic olefins[15–19] and asymmetric sulfoxides[20] have been achieved through separation of diastereoisomers of Pt(II) complexes. A stereospecific reaction of $PtCl_2$-(amine*) (C_2H_4) with some olefins has provided optically active olefins.[21] However, a successful extension of this type of reaction to resolution of phosphines is so far unknown. Resolutions of other monodentate racemic ligands with this system are currently under investigation.

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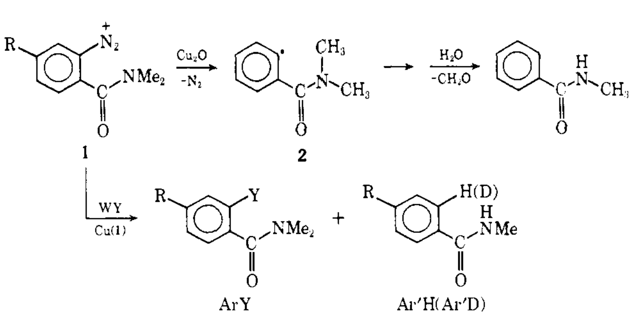
Isotope Effects after the Rate-Determining Step. The Role of Rotational Isomerism in a Hydrogen Transfer[1]

Sir:

Primary deuterium isotope effects are at present utilized in mechanistic studies very predominantly to gain information about rate-determining steps or preequilibria.[2] A potentially very informative use involves the study of competitive isotope effects in steps following the rate-determining step in order to discern whether or not a bond to hydrogen is being broken during the product-determining competition. In cases in which reactive intermediates are involved in hydrogen transfers, detailed mechanistic information can often be derived from such studies.

One application of this concept to the 1,5-hydrogen atom transfer which occurs in the radical **2**, produced by cuprous oxide promoted decomposition of the diazonium ion **1** (R = H), provided evidence that the rate of internal transfer is greater than that of rotation about the carbonyl CN bond but less than the rate of rotation about the methyl CN bond.[3]

We now report results which can be interpreted in terms of the behavior of the CC bond during this transfer. In the presence of a reagent WY capable of transferring an atom or radical group Y· to the aryl radical, two products ArY and Ar′H (the product of internal hydrogen atom transfer) may result. If the same experiment is then performed utilizing the completely methyl-deuterated diazonium ion, the relative yields of ArY and Ar′H (or Ar′D) may or may not change, due to an isotope effect.



Case A. If the external and internal transfers occur either in the same intermediate or in different intermediates whose rate of interconversion is greater than the rate of internal transfer, then the apparent isotope effect will equal the true isotope effect (rate of H transfer/rate of D transfer). The product-determining competition would be between external and internal transfer.

$$\text{apparent isotope effect} = \frac{\text{yield of Ar}'\text{H/yield of ArY (unlabeled)}}{\text{yield of Ar}'\text{D/yield of ArY } (d_6 \text{ experiment})}$$

Case B. If the two types of transfer occur in different intermediates and if the rate of internal transfer is much greater than the rate of conversion of the intermediate undergoing this transfer to the other intermediate, then there will be no change of yields upon deuteration (apparent isotope effect = 1); in this case the product-determining steps would not include the internal transfer.

The apparent isotope effect at 30° defined as above is in parentheses following the substrate on which it was determined, the medium, and the external atom Y: (1) **1** (R = H), water 1.15 *M* in $CuCl_2$ and 0.64 *M* in NaCl. Y = Cl from $CuCl_2$[4] (14.4); (2) **1** (R = OMe), water 2.19 *M* in $CuCl_2$ and 0.61 *M* in NaCl, Y = Cl from $CuCl_2$[4] (4.7); (3) **1** (R = H), methanol, Y = H from methanol[5] (4.8). The catalyst was cuprous chloride and the solutions were homogeneous for 1 and 2, while solid cuprous oxide was used in 3. However, the state of the catalyst has no apparent effect on the ratio of the reduction product to that of internal transfer since the ratio was the same when CuCl–HCl was used under homogeneous conditions, but in the latter case some contamination with aryl chloride occurred.

The value in 1 is quite reasonable for a combination of a primary and a secondary isotope effect based on the isotope effect determined on the diazonium ion in which each methyl group was dideuterated.[3,6] This

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(2) Reviews: V. Gold, *Chem. Brit.*, **6**, 292 (1970); M. Wolfsberg, *Annu. Rev. Phys. Chem.*, **20**, 449 (1969); W. H. Saunders, *Surv. Progr. Chem.*, **3**, 109 (1966); H. Simon and D. Palm, *Angew. Chem., Int. Ed. Engl.*, **5**, 920 (1966); J. Bigeleisen, *Science*, **147**, 463 (1965); L. C. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

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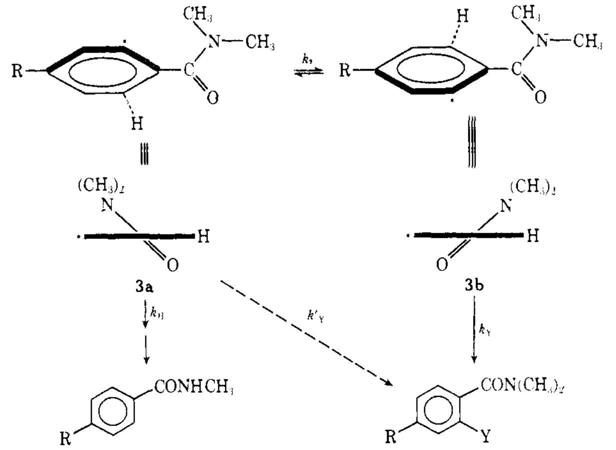
(5) Labeling studies indicate that the transferred hydrogen comes from the methyl group of the solvent.

(6) The apparent isotope effect in this example would be expected to be greater than 8.1 (this value has been corrected for the CH_2D and CD_3 content of the diazonium ion) found earlier[3] in water for decomposition of the diazonium ion in which both methyl groups are dideuterated, by a factor of about S^3 where *S* is the secondary isotope effect per deuterium atom. The value 8.1 is lower than the primary isotope effect by a factor *S* and the present value of 14.4 is greater than the primary effect

hydrogen transfer must then be close to the extreme of case A.

The large decreases in apparent isotope effects for 2 and 3 are not due to surprisingly large substituent and solvent influences, respectively, on the actual isotope effect for hydrogen transfer, since the corresponding diazonium salts labeled with two deuterium atoms in each methyl group (d_4) exhibit isotope effects in the appropriate solvents which are identical, within experimental error, with that of the tetradeuterated **1** (R = H) in water.[3,8] These are thus examples which are intermediate between cases A and B. In each of these two examples, one species must be undergoing predominant or exclusive external transfer while another must be undergoing predominant internal hydrogen atom transfer.

The most likely pair of species is **3a** and **3b** (only one enantiomer of each is shown) which are probably the two stable conformers of the intermediate radical about the CC bond. This latter assertion is based on (a) the crystal structures of benzamide and some analogs in which the aryl rings are canted from the plane of the amido groups by angles of 26–38°,[9] (b) evidence that various benzamides are nonplanar from spectroscopy,[10] complexing studies,[11] and model construction (the Fisher–Hirschfelder model of the coplanar form of *N*,*N*-dimethylbenzamide cannot be constructed even when one ortho hydrogen is removed), and (c) the expectation that the conformer in which the plane of the ring is perpendicular to that of the amido group is at an energy maximum due to the loss of resonance stabilization.



When R = OMe in aqueous cupric chloride or R = H in methanol, internal H transfer occurs from **3a** (the rate constant k_H probably involves the constant for bond rotation into a planar or nearly planar form as well as that for actual atom transfer), whereas Cl or external H transfer occurs in **3b**, although some external transfer from the more hindered **3a** cannot be ruled out. In these two reactions k_r is apparently of the same order of magnitude as k_H. The conversion of **3a** to **3b** requires the attainment of the perpendicular form in which resonance interaction between the ring and carboxamido group is minimized. Thus, the electron-donating *p*-methoxy substituent, by increasing this resonance stabilization, may decrease k_r.[12] It may also increase k_H by increasing the ease of achieving coplanarity.[12] A related explanation of the effect of this substituent is that it may decrease the average angle between the planes, thus, by steric hindrance, decreasing the contribution of k'_Y to the external transfer.

Studies on solvent and substituent effects in this system are planned. The application of this type of isotope effect study to other systems is well under way.

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by a factor S^2. The secondary effect then has the value of 1.2, which is in agreement with other α-secondary deuterium isotope effects in which a quaternary carbon is being converted to a trigonal carbon at that temperature.[7]

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(13) National Science Foundation Trainee.

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The Question of the Divergent Behavior of Singlet and Triplet Excited States of β,γ-Unsaturated Ketones. An Explanation Based on Spin Distribution[1]

Sir:

It has been demonstrated in several studies that cyclic and acyclic β,γ-unsaturated ketones show different reactions on direct, as contrasted with triplet-sensitized photolysis.[2–4] On direct irradiation a [1,3]-sigmatropic shift of the acyl group occurs to give an isomeric β,γ-unsaturated ketone.[5] The efficiency at this reaction normally is not reduced in the presence of typical triplet quenchers.[2–4,6]

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(1) The Application of Simple Theoretical Methods to the Solution of Chemical Problems. V. Paper IV: G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, **93**, 1058 (1971). This is also Part XXX of "The Photochemistry of Ketones in Solution." Part XXIX: D. I. Schuster, K. V. Prabhu, S. Adcock, J. van der Veen, and H. Fujiwara, *J. Amer. Chem. Soc.*, **93**, 1557 (1971).

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(5) This reaction has been known for some time, but only recently has it attracted mechanistic investigations. See, *e.g.*, G. Büchi and E. M. Burgess, *ibid.*, 82, 4333 (1960); D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963); W. F. Erman and H. C. Kretschmar, *J. Amer. Chem. Soc.*, **89**, 3842 (1967).

(6) The sole exception appears to be a bicyclo[3.2.0]hept-6-en-2-one where quenching of the 1,3-sigmatropic shift is observed and triplet energy transfer has been established.[7] Since the Stern–Volmer plot levels off at high quencher concentrations, it has been proposed that this [1,3] rearrangement occurs from both singlet and triplet excited states.[7] However, it now seems probable that the triplet excited state does take a different course to produce a thermally unstable cyclopropane[3] which would not have been detected under the analytical conditions used in the earlier study.[7] In this case, unlike other β,γ-unsaturated ketones,[2–4] intersystem crossing to give triplets is a significant process.