tion corresponding to **2** could be isolated from a reaction mixture of cobalt acetylacetonate and diethylaluminum monoethoxide in ether under argon atmosphere. The isolation of this complex suggests the presence of complex **2** in the catalyst solution as an active species of dimerization.

If the species **2** or **3** should exist in the system, further coordination of ethylene to the complex and ensuing insertion between ethyl–cobalt bonds are the most reasonable steps expected. Displacement of butene by ethylene through a butene–hydride intermediate (**6**) will regenerate **2**, and the cyclic process A will yield butene catalytically. Why ethane is formed is not clear at the moment, but a possible cause is hydrogen abstraction by the ethyl group from the *ortho* positions of the phenyl groups in the triphenylphosphine ligands.[13] The result of the independent isomerization experiment of 1-butene by **1** giving the same composition of butene isomers as obtained in the catalytic dimerization implies that another cycle, B, is operating in the dimerization reaction.

The propylene dimerization may proceed with a similar mechanism to that of ethylene dimerization involving the insertion of propylene molecules between the Co–H bond and the replacement of propylene dimers by propylene.

**Lyong Sun Pu, Akio Yamamoto, Sakuji Ikeda**
*Research Laboratory of Resources Utilization*
*Tokyo Institute of Technology, Meguro, Tokyo, Japan*
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## Solvolytic α-Deuterium Effects for Different Leaving Groups

*Sir:*

It has recently been found that *p*-methylbenzyl-α-$d_2$ chloride shows nearly the same isotope rate effect at 25° in 94% (by weight) trifluoroethanol–water (1.146 per D) and 70% trifluoroethanol–water (1.140) as has been reported for α-phenylethyl-α-*d* chloride at 25° in various ethanol–water mixtures (1.146–1.153).[1] This finding suggests that the α-deuterium effect for a limiting reaction is primarily a function of the leaving group and not of the structure of the particular alkyl group. Some typical solvolyses show effects about 3% smaller for ionization of the C–Br bond than of the C–Cl bond.[1]

Such isotope effects are related to changes in force constants at the position of isotopic substitution.[2] If the isotope effects and especially the relative bromide–chloride isotope effects do not depend on the particular alkyl group, it is appropriate to carry out model calculations on the methyl halides for which force fields obtained from vibrational data are available.[3] The conditions under which such calculations on the methyl halides should give significant information about the experimental systems have been discussed.[4]

With the use of the methyl halide force fields and geometries,[3] we have calculated, in the harmonic approximation, the equilibrium constant, $K_{ex}$, for $CH_3Cl + CH_2DBr \rightleftharpoons CH_2DCl + CH_3Br$ to be 1.037 at 25°. Detailed calculations indicate that this isotope effect reflects mainly the fact that force constants involving H–C–halide bending motion are larger in chloride than in bromide.

We designate by $R$ the ratio of $k_H/k_D$ in alkyl chloride solvolysis to the same quantity for an alkyl bromide. It is then straightforward to show, within the transition-state theory framework,[5] that $R = [(\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})_{Cl}/(\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})_{Br}][K_{ex}/K_{ex}^{\ddagger}]$ where $(\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})_{Cl}$ is the isotope effect, H/D, on the frequency corresponding to the reaction coordinate in the chloride and $K_{ex}^{\ddagger}$ is the exchange equilibrium constant analogous to $K_{ex}$ for the corresponding transition states but with the degree of freedom for the reaction coordinate missing.[6]

Calculations have been carried out with reasonable transition-state models which give essential agreement with the experimental $k_H/k_D$ values for the chlorides and bromides, respectively.[7] The transition-state force fields for the chloride and for the bromide were chosen to be the same, so, as expected, $K_{ex}^{\ddagger}$ is found to be very close to unity.[2] The ratio of $\nu_L^{\ddagger}$ ratios in the expression for $R$ is calculated to be 0.995 where the transition state has a planar $CH_3$ group, the C–halogen stretch force constant is set equal to −0.5 mdyn/Å, and all C–halogen stretch–interaction force constants are set equal to 0.0. This calculated value for the ratio of $\nu_L^{\ddagger}$ ratios is very close to that which one evaluates on the basis of methyl and halide fragment masses;[5] this ratio would be expected to be even closer to unity for larger molecules such as the α-phenylethyl halides.

Since, in our model, the $\nu_L^{\ddagger}$ ratios and $K_{ex}^{\ddagger}$ are very close to unity, the kinetic isotope effect, $R$, reduces essentially to $K_{ex}$, the equilibrium constant for isotopic exchange between the reactants. *We take the near agreement between the experimental value of R and the calculated value* $K_{ex}$ *to indicate that the force constants in the transition states of these limiting solvolysis reactions depend much less strongly on the particular halide than do the force constants of the reactants.*

In line with the above, it follows that the force constants for motion involving H–C–halogen bending are much more independent of halogen in the transition state than in the reactant. In our model calculations, reduction of force constants for this bending motion is the main contributor to the isotope effect.

Some time ago, Seltzer characterized as "normal" for limiting solvolysis an α-isotope effect of about 12% at 105° (or 15% at 25°),[8] and it was then possible to argue that the aqueous hydrolyses of alkyl halides and arylsulfonates were limiting only when the α-isotope effect did not differ from this value by more than a few per cent.[9] We can now make more precise mechanistic arguments by estimating how the effect will vary with the leaving group.

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(1) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

(2) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, 8, 325 (1964).

(3) J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, 45, 3383 (1966).

(4) M. J. Stern and M. Wolfsberg, *ibid.*, **45**, 4105 (1966). Briefly, these conditions are: (1) the force constant differences among the reactant halides at the hydrogen position must be the same as the corresponding differences among the larger reactant compounds, and (2) the force constant changes at these same positions between the methyl halide and the corresponding transition state must be correlated with similar differences in the systems studied experimentally.

(5) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 15 (1958).

(6) In the nomenclature of ref 5, $K_{ex}^{\ddagger} = f_{Cl}^{\ddagger}/f_{Br}^{\ddagger}$.

(7) Single-temperature isotope effect measurements do not, of course, determine uniquely the force constant changes between reactant and transition state.

(8) S. Seltzer, *J. Amer. Chem. Soc.*, 83, 2625 (1961).

(9) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 176 (1963).

The α-isotope effects characteristic of limiting solvolysis reactions of fluorides and iodides have not yet been experimentally established; on the basis that $K_{ex}{}^{\ddagger}$ is again unity we predict (using $(k_H/k_D)_{Br} = 1.125$) that the values per deuterium are ~1.22 and ~1.09, respectively. Unfortunately, no appropriate model force field is available for ionization of a C–O bond. However, α-deuterium effects in arenesulfonate solvolyses have been observed to be as large as 1.20,[10] so, if the analogy with halide solvolysis holds, the force constants for the HCO bending motion must be nearly as large as those for the corresponding HCF motion. We believe that α-deuterium effects much different from the values given above must at least in part involve different rate-determining steps.[11]

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[10] V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **86**, 945 (1964).

[11] NOTE ADDED IN PROOF. A referee has pointed out that a recent note (A. Guinot and G. Lamaty, *Chem. Commun.*, 960 (1967)) reports an unusually large isotope effect in the solvolysis of 1-chloro-1-phenylethane-2,2,2-$d_3$ in 95% ethanol. He suggests that the α effect may also be abnormally large in this solvent and that the present analysis based on an approximate maximum α effect of 1.15 (25°) for a limiting reaction may not be correct. Dr. Lamaty has informed us that measurements in 95% ethanol on 1-chloro-1-phenylethane-1-*d* give a $k_H/k_D$ ratio of 1.13 ± 0.02 at 50%, consistent with our interpretation; it appears that an artifact, the exact nature of which is under active investigation, caused the β-deuterium effect referred to above to be unusually large.

[12] National Science Foundation Graduate Fellow, 1964–1966; Indiana University Graduate School Fellow, 1966–1967; Public Health Service Predoctoral Research Fellow, 1967–1968.

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[14] Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel.

[15] Research performed under the auspices of the U. S. Atomic Energy Commission.

**V. J. Shiner, Jr., M. W. Rapp**[12]
*Department of Chemistry, Indiana University*[13]
*Bloomington, Indiana 47401*

**E. A. Halevi,**[14] **M. Wolfsberg**
*Chemistry Department, Brookhaven National Laboratory*[15]
*Upton, New York 11973*

*Received July 8, 1968*

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## Tris(triphenylphosphine)ruthenium Nitrogen Dihydride

*Sir:*

Preparations of $[(NH_3)_5RuN_2]^{2+}$ [1–3] and of a tris(triphenylphosphine)cobalt nitrogen complex[4–7] by routes involving facile reactions of molecular nitrogen have been reported. More recently a communication revealed that passage of nitrogen through a benzene solution of $[(C_6H_5)_3P]_4RuH_2$ appeared to result in the formation of a triphenylphosphine ruthenium nitrogen complex, although the complex could not be isolated.[8] Working along similar lines we have found that a nitrogen complex can be easily isolated from the reaction of $[(C_6H_5)_3P]_3RuHCl$[9] with triethylaluminum and nitrogen in ether. The complex, $[(C_6H_5)_3P]_3Ru(N_2)H_2$, readily loses nitrogen when treated with additional triphenylphosphine. This observation probably explains the failure to isolate a nitrogen complex from the tetrakis(triphenylphosphine)ruthenium solutions.

$[(C_6H_5)_3P]_3Ru(N_2)H_2$ is an air-sensitive solid which is almost white when pure but frequently is tan or red-brown. It can be recrystallized from benzene–hexane in a nitrogen atmosphere and is stable indefinitely at room temperature. It darkens above 140° and melts at 185°.

*Anal.* Calcd for $[(C_6H_5)_3P]_3Ru(N_2)H_2$: C, 70.9; H, 5.2; N, 3.1; P, 10.1; Ru, 10.9. Found: C, 70.9; H, 5.3; N, 3.2; P, 10.2; Ru, 10.7.

The infrared spectrum (Nujol mull) has a strong sharp band at 2147 cm$^{-1}$ assigned to the coordinated nitrogen moiety and bands of moderate intensity at 1947 and 1917 cm$^{-1}$ assignable to ruthenium–hydrogen stretching. The assigned composition is further supported by reaction of the complex with hydrogen chloride.

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 \xrightarrow{HCl} [(C_6H_5)_3P]_3RuCl_2 + \underset{81\%}{N_2} + \underset{94\%}{2H_2}$$

The nitrogen in $[(C_6H_5)_3P]_3Ru(N_2)H_2$ is reversibly displaced by ammonia and by hydrogen, forming $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ and $[(C_6H_5)_3P]_3RuH_4$, respectively. Characterization of the latter product as a tetrahydride is supported by sequential reactions with triphenylphosphine and hydrogen chloride.

$$[(C_6H_5)_3P]_3RuH_4 \xrightarrow{(C_6H_5)_3P} \underset{84\%}{H_2} + [(C_6H_5)_3P]_4RuH_2 \xrightarrow{HCl} [(C_6H_5)_3P]_4RuCl_2 + \underset{83\%}{2H_2}$$

Solutions of the nitrogen complex are stable in a nitrogen atmosphere but slowly lose nitrogen in an argon atmosphere. A tetrahydrofuran solution initially containing both $[(C_6H_5)_3P]_3Ru(N_2)H_2$ and $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ in an argon atmosphere slowly deposits a yellow crystalline solid. Elemental analysis reveals this has the composition $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$. Insolubility has precluded molecular weight measurements; there is no infrared absorption indicative of ruthenium–hydrogen bonds.

*Anal.* Calcd for $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$: C, 61.2; H, 4.8; N, 2.4; P, 8.8. Found: C, 61.0; H, 5.2; N, 2.3; P, 8.2.

It is postulated that this cluster is a trigonal pyramid consisting of a $[(C_6H_5)_3P]_2Ru$ moiety (from the nitrogen complex *via* loss of triphenylphosphine, nitrogen, and hydrogen) and three $(C_6H_5)_3PRuNH_3$ moieties (from the ammonia complex *via* loss of triphenylphosphine and hydrogen).

It was reported previously that the phenyl groups in $[(C_6H_5)_3P]_3Co(N_2)H$ undergo deuterium–hydrogen exchange at the *ortho* positions.[10] A similar phenomenon is found in the ruthenium system. In an equilibration experiment, 84% of the theoretical amount of hydrogen expected from complete exchange of all *ortho* hy-

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