too small to be consistent with rate-determining proton switch but is consistent with the suggested mechanism.

Our conclusions pertinent to the preassociation mechanism for the acid-catalyzed reactions are entirely in accord with the recent observations of Cox and Jencks.[9] On the basis of a nonlinear Brønsted plot and a sharp maximum in solvent deuterium isotope effects for general acid catalyzed methoxyaminolysis of phenyl acetate, these workers have concluded that the general acid catalyzed pathway for monofunctional acids more acidic than $pK_a = 4$ occurs by the preassociation mechanism.

References and Notes

(1) Supported by Research Grant CHE 77-09496 from the National Science Foundation.
(2) A. C. Satterthwait and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 7018, 7031 (1974).
(3) W. P. Jencks, *Acc. Chem. Res.*, **9**, 425 (1976).
(4) Z. Bilkadi, R. de Lorimier, and J. F. Kirsch, *J. Am. Chem. Soc.*, **97**, 4317 (1975). This limit refers specifically to methyl formate and may differ significantly for 4-methoxyphenyl formate.
(5) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and W. S. Bowman, Ed., Van Nostrand-Reinhold, Princeton, N.J., 1970.
(6) H. G. Bull, K. Koehler, T. C. Pletcher, J. J. Ortiz, and E. H. Cordes, *J. Am. Chem. Soc.*, **93**, 3002 (1971).
(7) L. do Amaral, M. P. Bastos, H. G. Bull, J. J. Ortiz, and E. H. Cordes, *J. Am. Chem. Soc.*, in press.
(8) Statistical Package for the Social Sciences, Version 6.5. Vogelbach Computing Center, Northwestern University, Evanston, Ill, 1976.
(9) M. M. Cox and W. P. Jencks, *J. Am. Chem. Soc.*, **100**, 5956 (1978).

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Rates of Degenerate 1,2-Hydride and 1,2-Methide Shifts from the Carbon-13 Nuclear Magnetic Resonance Spectra of Tertiary Alkyl Cations

Sir:

The 1,2 shift of hydride or methide is the most common and important rearrangement of carbonium ions. Until now, all simple ions for which this shift is degenerate have given sharp, averaged NMR spectra at temperatures as low as -160 °C.[1,2] Kinetic line-shape effects have been observed only for cations with special stabilization, such as the norbornyl cation,[3] the benzenonium ion,[4] and their derivatives.[3,4] Because line broadening in the fast exchange limit is proportional to frequency squared, we have been able to observe line broadening in, and measure rates for degenerate 1,2 shifts from, the high-field (67.9 MHz) ^{13}C NMR spectra of I–VI.

Solutions of I–IV,[1,2] VI,[1,2] and a 50:50 mixture of V[2h] and VII[2h] were prepared[5] from the corresponding alcohols in 50:50 SO_2ClF/SO_2F_2; external CD_3OCD_3/CCl_2F_2 or
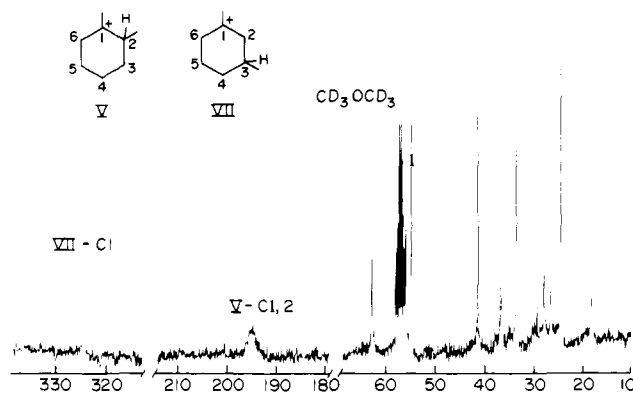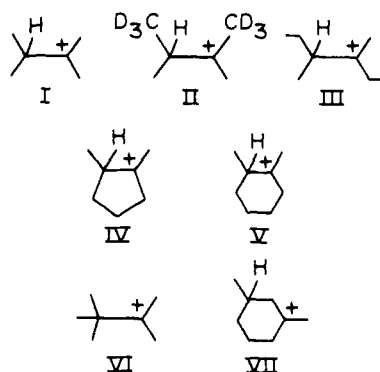

Figure 1. 67.9-MHz ^{13}C NMR spectrum of a 50:50 mixture of V and VII at -135 °C.

Table I. Experimental Line Widths and Rates

compd	temp, °C	W, Hz[a]	$k/10^7$, s^{-1}
I	-119	4	14
	-128	12	4.6
	-138	18	3.1
II	-119	2	28
	-125	2	28
	-130	5	11
	-135	10	5.6
	-138	13	4.3
III	-116	225	0.25
IV	-126	2	28
	-135	6	9.2
	-135	5	11
	-139	18	3.1
V	-119	11	5.0
	-122	12	4.6
	-126	34	1.6
	-128	41	1.4
	-135	125	0.46
	-137	148	0.40
VI	-110	2	28
	-114	5	11
	-125	16	3.5
	-129	34	1.6
	-136	65	0.85

[a] See text for definition of W.

CD_3OCD_3/SO_2F_2 were used as lock substance and reference; temperatures were measured to ± 2 °C using the temperature dependence of the chemical shifts of a separate sample of 2-chlorobutane.[6,7] Rates were computed according to the fast exchange limit approximation,[8] $k = (\pi/2) \times (\Delta^2/W)$, where Δ is the chemical-shift separation, in hertz, between the nuclei that are averaged, and W is the width of the broadened peak minus the natural line width. Estimates of Δ range from 261 to 278 ppm.[1,2,9] The value 277 ppm[2a] (18803 Hz) was used throughout, since obtained thermodynamic values are insensitive to Δ. The width of the averaged methyl peak was used as the natural line width.

The mixture of V and VII was prepared to determine whether we might be observing only relaxation broadening of the averaged cation-methine (C-1–C-2) peak, as a result of T_1 shortening induced by chemical-shift anisotropy.[10] This process would broaden the C-1 peak of VII (δ 325 ppm) more than any other. However, in the ^{13}C NMR spectrum[11] of V and VII at -135 °C (Figure 1), only the peak at δ 195 ppm (C-1–C-2 of V) is broadened. Therefore, chemical-shift anisotropy is not the cause of broadening.

The line widths and rates for I–VI are presented in Table I. We have not fit the data to the Arrhenius equation, because, over the narrow range of accessible temperatures, systematic deviations could lead to large errors in E_a and log A. The free

energies of activation[12] are, for I, $\Delta G^{\ddagger} = 3.1 \pm 0.1$ kcal/mol at -138 °C; for II, $\Delta G^{\ddagger} = 3.0 \pm 0.1$ kcal/mol at -138 °C; for III, $\Delta G^{\ddagger} = 4.4 \pm 0.2$ kcal/mol at -116 °C; for IV, $\Delta G^{\ddagger} = 3.1 \pm 0.1$ kcal/mol at -139 °C; for V, $\Delta G^{\ddagger} = 3.7 \pm 0.1$ kcal/mol at -137 °C; and for VI, $\Delta G^{\ddagger} = 3.5 \pm 0.1$ kcal/mol at -136 °C. Error limits are standard deviations.

The inverse β secondary deuterium isotope effect ($k_{\mathrm{I}}/k_{\mathrm{II}} \approx 0.7$ at -138 °C) indicates that methyl C–H force constants are greater in the transition state than in the ground state. This implies less hyperconjugation in the transition state than in the ground state.

The rate of the methide shift in VI is between those of the hydride shifts in I and V, reflecting the energy difference between a proton bridge and a protonated cyclopropane, and the conformation change accompanying rearrangement in the six-membered ring. The still lower rate in III may indicate a steric barrier to rotation about the C-3–C-4 bond.

We see no broadening in the ^{13}C NMR spectrum of 2-butyl cation at -140 °C. Assuming that Δ is 277 ppm, the lower limit for the rate is 4×10^9 s^{-1} and the upper limit for $\Delta G^{\ddagger}$ is 2.4 kcal/mol.

References and Notes

(1) M. Saunders, L. Telkowski, and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8070 (1977); M. Saunders, M. H. Jaffe, and P. Vogel, *ibid.*, **93**, 2558 (1971); M. Saunders and P. Vogel, *ibid.*, **93**, 2559, 2561 (1971).
(2) (a) G. A. Olah and D. J. Donovan, *J. Am. Chem. Soc.*, **99**, 5026 (1977); (b) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (c) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967); (d) G. A. Olah, J. R. Demember, A. Commeyras, and J. L. Brides, *ibid.*, **93**, 459 (1971); (e) D. M. Brouwer, *Recl. Trav. Chim. Pay-Bas*, **87**, 210 (1968); (f) D. M. Brouwer and J. A. van Doorn, *ibid.*, **89**, 88 (1970); (g) H. Hogeveen and C. H. Gaasbeek, *ibid.*, 88, 1305 (1969); (h) A. P. W. Hewett, Ph.D. Thesis, Yale University, 1975.
(3) A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973); R. P. Haseltine, E. Huang, K. Ranganayakulu, T. S. Sorensen, and N. Wong, *Can. J. Chem.*, **53**, 1876 (1975).
(4) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Am. Chem. Soc.*, **92**, 2546 (1970); B. B. Derendyaev, V. I. Mamatyuk, and V. A. Koptyug, *Tetrahedron Lett.*, 5 (1969); W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, and W. R. Edwards, *Tetrahedron*, **4**, 178 (1958); D. M. Brouwer, C. MacLean, and E. L. Mackor, *Discuss. Faraday Soc.*, **39**, 121 (1965).
(5) (a) M. Saunders, D. Cox, and W. Olmstead, *J. Am. Chem. Soc.*, **95**, 3018 (1973). (b) Reference 2h, pp 97–104. (c) A detailed description of our technique for generation of ion solutions is being prepared for publication.
(6) H. J. Schneider and W. Freitag, *J. Am. Chem. Soc.*, **98**, 478 (1976).
(7) M. R. Kates, Ph.D. Thesis, Yale University, 1978, pp 123–128.
(8) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).
(9) J. R. Lloyd, unpublished results.
(10) (a) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, 1971, p 59; (b) J. A. Berden, P. R. Cullis, D. I. Hoult, A. C. McLaughlin, G. K. Radda, and R. E. Richards, *Fed. Eur. Biochem. Soc. Lett.*, **46**, 55 (1974); (c) T. C. Farrar, S. J. Druck, R. R. Shoup, and E. D. Becker, *J. Am. Chem. Soc.*, **94**, 699 (1972); (d) G. C. Levy, *J. Chem. Soc., Chem. Commun.*, 47 (1972); (e) A. P. W. Hewett, Ph.D. Thesis, Yale University, 1975, pp 79–80.
(11) Spectra were taken in the Bruker HX270.
(12) Rate = $(kT/h) \exp(-\Delta G^{\ddagger}/RT)$.
(13) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Am. Chem. Soc.*, **90**, 6882 (1968).

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Catalytic Decarbonylation of Aldehydes

Sir:

Stoichiometric homogeneous decarbonylation of aldehydes using transition metal complexes of *monodentate* tertiary

phosphine ligands such as RhCl(PPh$_3$)$_3$,[1-3] [Rh(PPh$_3$)$_2$(solvent)$_n$]$^+$,[4] and [Ru$_2$Cl$_3$(PEt$_2$Ph)$_6$]$^+$ [5] is now well established. Of these, RhCl(PPh$_3$)$_3$ (1) has received the most study and has proved useful as a reagent in organic synthesis.[6,7] The basic reaction is thought to occur through the three-coordinate intermediate [RhCl(PPh$_3$)$_2$]:

$$\text{RCHO} + [\text{RhCl(PPh}_3)_2] \rightarrow \text{RH} + t\text{-}[\text{RhCl(CO)(PPh}_3)_2] \quad (1)$$
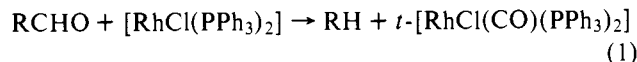
Small amounts of alkenes and H$_2$ are also formed from higher saturated aldehydes; for example, 14% 1-hexene is produced from heptanal.[2] The mechanism for the stoichiometric decarbonylation is presumably similar to that proposed for acyl halides.[7,8] The reaction cannot be made sufficiently catalytic at useful temperatures because t-RhCl(CO)(PPh$_3$)$_2$ does not lose carbon monoxide and the active species [RhCl(PPh$_3$)$_2$] cannot be regenerated thermally[9] or photochemically.[10] The decarbonylation reaction can be made catalytic for high boiling aldehydes with 1 or t-RhCl(CO)(PPh$_3$)$_2$ (vide infra) at temperatures >200 °C,[6] but CO loss is proposed[2] to occur from the acyl intermediate, which results from oxidative addition of aldehyde to t-RhCl(CO)(PPh$_3$)$_2$. Results reported in this communication will show that clean homogeneous *catalytic* decarbonylation of aldehydes using *cationic* rhodium(I) complexes of *chelating* diphosphine ligands occurs at temperatures considerably lower than with 1 and with long-term catalyst stability.

Since a key step in catalytic decarbonylation is the expulsion of coordinated CO and regeneration of the active catalyst, it seemed reasonable to explore the reaction chemistry of aldehydes with *cationic* complexes of *chelating* diphosphine ligands. Such complexes should bind CO much less strongly than t-RhCl(CO)(PPh$_3$)$_2$ owing to decreased Rh–CO π back-bonding. This should result because the cationic complexes are less electron rich and likely to have trans rhodium–phosphorous stereochemistry. Accordingly, the complexes [Rh(dppe)$_2$]Cl (2) and [Rh(dppp)$_2$]Cl (3) where dppe = 1,2-bis(diphenylphosphino)ethane and dppp = 1,2-bis(diphenylphosphino)propane were synthesized[11] and reacted with benzaldehyde and heptanal under several conditions of temperature and solvent.[13] In a typical experiment ~20 mg of 2 or 3 was dissolved in 30 mL of a solution consisting of either neat aldehyde or ~2 mL of aldehyde in *m*-xylene or toluene. The homogeneous solution was stirred at constant temperature and continuously purged with purified nitrogen gas. The products were collected continuously in a trap connected to the end of a reflux condenser and quantitatively analyzed by GLC. The identity of the organic products was verified by comparison of GLC retention times with those of authentic samples.[14] The results are shown in Table I. All experiments were repeated several times and the data reported in Table I are typical. The results of experiments using 1 or t-RhCl(CO)(PPh$_3$)$_2$ are also presented in Table I for comparison purposes and because these data have not been previously reported in the literature. Control experiments were run under identical conditions except without the rhodium catalyst present and *no* decarbonylation products were observed.

It is apparent that the catalytic activities using 2 or 3 are much greater than those using 1. Inded, catalytic activities even approaching 100 with 1 or t-RhCl(CO)(PPh$_3$)$_2$ are achieved only at temperatures in excess of 230 °C.[2] Additionally, 2 and 3 exhibit long-term stability. Reactions have been run for as long as 1 week with constant catalytic activities and turnover numbers of 100 000 have been achieved, although much higher turnovers are certainly possible. The per cent yield based on aldehyde is 100% for benzene production from benzaldehyde. Hexane is the only volatile product obtained from heptanal. Although it is desirable to achieve catalytic decarbonylation

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