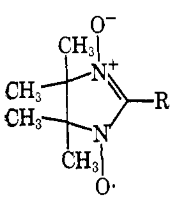
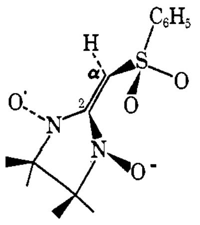


I



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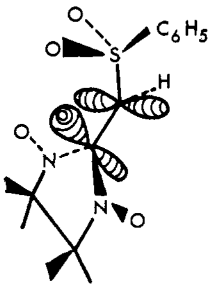
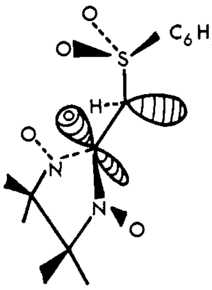


IIb



IIc

son of the nitrogen coupling constants of II with other nitronyl nitroxides demonstrates unexpectedly low charge delocalization into the heterocyclic ring. Thus a_N (in 3 *N* KOH) increases with the electron-donating ability of the side chain in the series I, R = CH_2SO_2Ph (7.77 G),[8] C_6H_5(8.10), CH_3 (8.2), *p*-$C_6H_4O^-$ (8.29), and O^- (8.77).[7c] By comparison a_N(av) for II was 8.55 G despite the likelihood that the carbanionic side chain has the strongest electron-donating properties in the series. (3) The high rate of the temperature-dependent process (Table I) demands minimal double bond character in the C_2–C_α bond and high charge localization at C_α. (4) Decreasing the solvent polarity should favor charge delocalization into the nitronyl nitroxide ring in IIa and thus decrease the symmetrization rate and increase a_N. In fact, the rate increased and a_N(av) decreased (Table I).

Table I. Activation Parameters for Symmetrization of II[a]

Vol % H_2O in EtOH[b]	a_N (av)	δa_{max}, G	T_c,[c] °C	$10^{-6}k_c$ sec^{-1}	ΔE_a, kcal/mol	A, sec^{-1}
30	8.35	~1.0	34	6.2		
50	8.35	1.45	58	9.0	6.0	8×10^{10}
70	8.41	1.75	73	10.9	4.6	9×10^{9}
90	8.50	2.00	82	12.4	2.4	4×10^{8}

[a] Calculated from temperature variation of δa (= $a_{N1} - a_{N2}$) at 9.5×10^9 Hz by the method of H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). [b] 3 *N* in KOH. [c] Coalescence temperature (±2°).

An alternative to IIa that might account for the different environments of the two nitrogens is IIb. Related planar sulfonyl carbanion geometries having restricted rotation about the C–S bond have previously been proposed to explain asymmetry in these substances.[1,4] Although completely definitive evidence excluding IIb is lacking, careful examination of molecular models[9] suggests that rotation about the C_2–C_α bond in IIb may be insufficiently hindered to significantly interfere with free rotation. However, pyramidal carbanion IIc would be sufficiently hindered and accommodates all the observations. Charge delocalization toward the nitronyl nitroxide would be small in IIc, due to sp^3 hybridization at C_α, and the small hyperfine coupling of C_α-H is consistent with the probable orientation of this hydrogen only slightly out of the radical plane. Further, *the effect of solvent on the symmetrization rate exactly parallels the solvent effects on amine inversion rates.*[10] Thus decreases in solvent hydrogen-bonding ability in each case cause higher symmetrization rates, frequency factors, and activation energies which are consistent with increased delocalization of the free electron pair in the transition state.

If structure IIc is correct, the observed rates probably correspond to pyramidal inversion at C_α. Molecular models indicate that rotation about C_α–C_2 is prohibited unless there is concomitant flattening at C_α or rotation about C_α–S, and rotation about the latter bond would destroy the electrostatic interactions that are considered necessary for stabilization of possible pyramidal configurations of α-sulfonyl carbanions.[1,3,4] However, if structure IIb were correct, partial twisting about the C_α–S bond might suffice to remove the rotational barrier about C_α–C_2. The observed rates would then only represent maximum values for rotation of a planar carbanion about the C–S bond.

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(8) Corrected value based on measured coupling of 7.85 G in water.

(9) Corey–Pauling–Koltun models with 120° valence angles at C_α.

(10) (a) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958); (b) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960).

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The Effect of Bending Vibrations on the Magnitude of Hydrogen Isotope Effects[1]

Sir:

Both theory[2] and experiment[3] clearly indicate that hydrogenic stretching vibrations in the transition state play an important role in fixing the magnitude of hydrogen isotope effects on proton-transfer reactions. Although it is recognized that transition-state bending vibrations might also exert a strong influence, little definite information is available. We wish, therefore, to present the results of an experiment which show a remarkable isotope effect lowering directly ascribable to transition-state bending vibrations, and from which an approximate value of the frequency of these vibrations may be deduced.

In all proton-transfer reactions for which isotope effects have been measured so far, the proton donor

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(1) This research was supported by a grant (GP 6580) from the National Science Foundation to the Illinois Institute of Technology.

(2) (a) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); J. Bigeleisen, *Pure Appl. Chem.*, **8**, 217 (1964); A. V. Willi and M. Wolfsberg, *Chem. Ind.* (London), 2097 (1964); R. P. Bell, *Discussions Faraday Soc.*, **39**, 16 (1965); (b) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.*, *B*, 985 (1967).

(3) (a) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* (London), **A294**, 273 (1966); J. L. Longridge and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1292 (1967); (b) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *ibid.*, **90**, 4174 (1968).

has been a polyatomic molecule. In such systems, effects of transition-state bending motion are obscured by counter-balancing effects of the initial-state bending vibrations. Very recently, however, it has been demonstrated that hydrogen fluoride, a diatomic molecule with no bending vibrational modes, behaves as a normal proton donor in aqueous solution and that rates of proton transfer from this acid to ethyl vinyl ether can be evaluated easily and accurately.[4] We have therefore determined the isotope effect on this reaction by measuring its rate in D_2O solution.

Hydrogen fluoride undergoes two equilibrium reactions in aqueous solution, ionization as an acid (eq 1) and association with fluoride ion to form hydrogen bifluoride (eq 2). The latter, however, is not catalytically active in the hydrolysis of ethyl vinyl ether,[4] and the rate law for this reaction therefore consists only of terms in hydrogen fluoride and hydronium ion (eq 3). Unfortunately, it is not possible, as it was for H_2O solution,[4] to evaluate the relative contributions of these two terms by straightforward calculation of solution compositions, for the necessary equilibrium constants, K_1 and K_2, are not known for D_2O solution. We therefore used an indicator method employing 2,4-dichloroaniline, which is known to measure H_3O^+ concentration in H_2O solutions of hydrogen fluoride accurately,[4] to determine D_3O^+ concentrations. These indicator data also provided a rough estimate of K_2 which enabled us to make allowance for the small (*ca.* 2%) change in DF concentration produced by the reaction of eq 2 over that effected by the ionization according to eq 1. Using the known value of $k_{D_3O^+}$,[5] we could then evaluate k_{DF} as $(2.01 \pm 0.02) \times 10^{-2}$ M^{-1} sec^{-1} at 24.9°. Combined with k_{HF},[4] this gives 3.35 ± 0.05 as the isotope effect on proton transfer from hydrogen fluoride to ethyl vinyl ether.

$$DF + D_2O \underset{}{\overset{k_1}{\rightleftarrows}} D_3O^+ + F^- \qquad (1)$$

$$DF + F^- \overset{k_2}{\rightleftarrows} DF_2^- \qquad (2)$$

$$-d[S]/[S]dt = k_{D_3O^+}[D_3O^+] + k_{DF}[DF] \qquad (3)$$

This isotope effect is very small; it is less than one-quarter of the value estimated for uncompensated loss of the (very large) stretching vibration of hydrogen fluoride. It seems unlikely that very much of this lowering can be due to a "symmetrical" stretching vibration in the transition state whose frequency is sensitive to the mass of the hydrogen being transferred. The value of Brønsted's α for this reaction[6] as well as solvent isotope effects in H_2O–D_2O mixtures[5] and more directly measured secondary isotope effects[6] all point to a transition state in which this hydrogen is held with approximately equal force by the two bases between which it is moving. This reasoning is supported by the fact that the isotope effect for this reaction catalyzed by the hydronium ion has a near-maximum value[3b] and that for catalysis by formic acid is also large.[5] It is reasonable to conclude, therefore, that the presently measured isotope effect is as small as it is largely because the absence of initial-state bending vibrations leaves the effect of bending motion in the transition state uncompensated.

If all of this decrease in isotope effect is assigned to transition-state bending vibrations, and if it is further assumed that protium and deuterium frequencies are related in the simple way $\nu_H = \nu_D\sqrt{2}$, a frequency of approximately 1100 cm^{-1} can be calculated for the two degenerate transition-state bending modes. This value is in remarkably good agreement with that (1080 cm^{-1}) calculated from a simple electrostatic model for proton transfer,[7] and it also falls in the range estimated for transition states by analogy with stable molecules.[2b] A frequency of 1100 cm^{-1}, moreover, is not very different from that of hydrogenic bending vibrations in many molecules; this suggests that transition-state and initial-state bending frequencies might in general be quite well matched, and this would account for the success in predicting maximum values of isotope effects enjoyed by the commonly used approximation which takes into consideration only the stretching vibration of the initial state.

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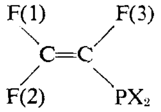
A Sign Inversion in the Geminal Phosphorus–Fluorine Coupling Constant

Sir:

It is now well established that the P–C–H coupling constant undergoes a sign change when a phosphine is quaternized or enters into complex formation.[1] By contrast it has been considered hitherto that the P–C–F coupling constant is unlikely to be subject to a sign inversion.[1c,2] It is the purpose of this communication to present some evidence to the contrary. As such this appears to be the first report of a sign change in a coupling constant involving phosphorus and fluorine.

The crucial point in our argument is illustrated in Figure 1. Irradiation of the lowest field line of the F(3) resonance of $CF_2{=}CFPCl_2$ causes lines 3 and 7 of the F(2) resonance (Figure 1b) to split into doublets, thus indicating that the P–C–F coupling is opposite in sign to the *cis*-P–C–C–F coupling. However, in $CF_2{=}CFPF_2$ irradiation of the lowest field line of the F(3) resonance causes perturbations in triplets 1 and 5



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