is reduced by about one-third. The effects of these additives on the TME radical ion agree qualitatively with the results obtained by Shida and Hamill[1] for radical cations.

The value of the coupling constant, $a_H = 16.7$ G, lends further qualitative support for the presence of the TME radical cation. According to Symons[7] the coupling constant of a β proton is related to the Q_β value by

$$a_\beta = Q_\beta\left(\rho_C{}^0 - \frac{Na_\beta}{502}\right)$$

where $\rho_C{}^0$ is a formal charge density on the α carbon ($+0.5$), and N is the number of β protons. For TME$^+$ we obtain $Q_\beta = 55.6$ G. Although not in quantitative agreement with the data of Hulme and Symons,[8] this result approaches the large Q values expected by these authors for organic radical cations.

By comparison of the center of the 13-line spectrum with that of the methyl radical spectrum (obtained by radiolysis of CH_3I in the TME–3-MP system), the g value was found to be 2.0025 ± 0.0003. Unfortunately, there exists no theory for the shift of g values for alkyl-substituted hydrocarbon radical ions or experimental data with which this value could be compared. It is, however, interesting that within the relatively large limit of error the g value for the proposed TME$^+$ coincides with the corresponding values for aromatic cations.[9]

It is interesting to note that, at higher TME concentrations under otherwise the same conditions as given for Figure 1a, the spectrum of Figure 1b is obtained showing an average line separation of 7.8 G. This is about one-half of the separation found for TME$^+$. In the absence of CO_2 this species is also sensitive to optical and thermal bleaching. Possibly, at higher concentrations the formation of a dimeric radical cation $(TME)_2{}^+$ occurs as discussed by Edlund, *et al.*,[10] for benzene–silica gel systems.

Acknowledgment. We wish to thank Professor Milton Burton for helpful discussions.

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[9] B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

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[12] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-647.

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Received November 8, 1968

Studies of Stable Free Radicals. IV. The Origin of Asymmetry and Rate of Symmetrization of a Spin-Labeled α-Sulfonyl Carbanion

Sir:

It is recognized that asymmetry at carbon atoms bearing a sulfone grouping is often retained in the corresponding α-sulfonyl carbanion.[1] However, the absolute rates of racemization of these asymmetric carbanions are unknown, and with one exception only rates relative to protonation have been measured.[2] Further, the reason for the asymmetry remains in dispute. Evidence has been given in support of pyramidal carbanions,[3] but there are cogent arguments that maintenance of asymmetry results primarily from coulombic restrictions to rotation in α-sulfonyl carbanions, whether planar or pyramidal.[4] We present here evidence bearing on these points.

Treatment of the stable radical I, R = CH_2Cl,[5,6] with aqueous sodium phenylsulfinate and potassium iodide yielded I, R = $CD_2SO_2C_6H_5$.[6] This sulfone gave typical nitronyl nitroxide esr spectra of five triplets produced by coupling with two equivalent nitrogens and two α hydrogens ($a_N = 7.85$, $a_H = 1.77$ G, H_2O). Dissolution of this radical in aqueous 6 *N* KOH produced solutions of II having nine-line esr spectra resulting from coupling with two nonequivalent nitrogens [a_N(av) = 8.55 G]. No additional coupling was evident except for expected line broadening (~0.9 G) from unresolved coupling with the methyl hydrogens (~0.2 G).[7b] Neutralization of this solution regenerated the original five-triplet pattern. In weakly alkaline deuterium oxide the sulfone gave the expected five-singlet spectrum of I, R = $CD_2SO_2C_6H_5$, and addition of more alkali again gave the nine-line pattern. Slightly diminished line widths (~0.75 G) in this spectrum suggest possible coupling of ~0.2 G by the α hydrogen in II. Warming of alkaline solutions of II caused collapse of the nine-line pattern to five lines expected by averaging of the spin densities on the nonequivalent nitrogens. This averaging was not produced by proton exchange since the residual five-triplet pattern observed in less basic, incompletely ionized solutions of the sulfone failed to collapse on heating.

The nonequivalence of the nitrogens in II must arise from asymmetric solvation or polarization of the normally symmetric nitronyl nitroxide grouping by an asymmetrically distributed charge in the side chain. Possible structures which could account for this asymmetry include IIa, IIb, and IIc, each of which would be expected to have nonequivalent nitrogens provided there is restricted rotation about the C_2–C_α bond. Among these alternatives, planar carbanion IIa appears unlikely by several considerations. (1) Attachment of the α hydrogen directly to the radical π-electron system in IIa should cause stronger α-hydrogen hyperfine interaction than the <0.2 G observed (*cf.* I, R = $CH{=}CHC_6H_5$,[5,6] $a_{H\alpha} = a_{H\beta} = 1.5$ G). (2) Compari-

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[1] (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 105; (b) D. J. Cram, W. D. Nielsen, and B. Rickborn, *J. Am. Chem. Soc.*, **82**, 6415 (1960); (c) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).

[2] Rates of symmetrization of the configurationally constrained 2,2-dimethyl-1-phenylsulfonylcyclopropyl anion in DMSO–THF have recently been measured by nmr. However, ion-pair dissociation rather than inversion or rotation is probably rate controlling in this solvent: A. Ratajczak, F. A. L. Anet, and D. J. Cram, *ibid.*, **89**, 2072 (1967).

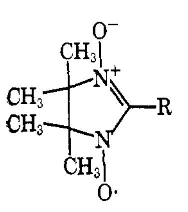
[3] D. J. Cram and A. S. Wingrove, *ibid.*, **84**, 1496 (1962); (b) *ibid.*, **85**, 1100 (1963).

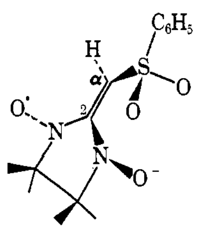
[4] (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962); (b) E. J. Corey and T. H. Lowry, *ibid.*, 793, 803 (1965).

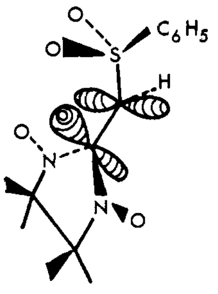
[5] See ref 7 for method of synthesis of nitronyl nitroxides.

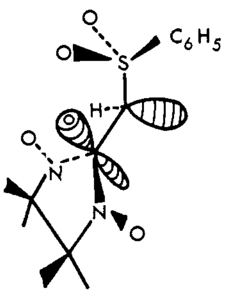
[6] Satisfactory combustion analysis and mass spectrum.

[7] (a) J. H. Osiecki and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 1078 (1968); (b) D. G. B. Boocock, R. Darcy, and E. F. Ullman, *ibid.*, **90**, 5945 (1968); (c) D. G. B. Boocock and E. F. Ullman, *ibid.*, **90**, 6873 (1968).


I


II


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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Received October 16, 1968

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.

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