celerated by ROH. This is shown clearly by the following experiments. Triphenylmethane (0.44 *M*) in a solution of 0.33 *M* $\mathrm{CH_3SOCH_2^-K^+}$ in DMSO has an nmr spectrum which is the superposition of the spectra of $\mathrm{Ph_3CH}$ and $\mathrm{Ph_3C^-K^+}$. The methine peak is not broadened. Irradiation of the main DMSO peak causes no decrease in the methine height (the ^{13}C satellite does diminish as expected).[7-9] Thus, exchange is slow under these conditions. However, in a DMSO solution containing 0.44 *M* $\mathrm{Ph_3CH}$, 0.29 *M* $\mathrm{CH_3SOCH_2^-K^+}$, and 0.13 *M* ROH, the ratio of $\mathrm{Ph_3C^-K^+}$ to $\mathrm{Ph_3CH}$ is smaller, indicating a less basic medium, and both the aromatic and methine peaks are broadened. The broadening of the methine is shown to be due ultimately to exchange with DMSO by irradiation of the main DMSO peak which now causes the methine to diminish to about 10% of its former height. Consequently, in these solutions exchange is fast. We estimate the acceleration to be at least as great as that observed for DMSO itself. Broadening of the methine peak persists even when very little $\mathrm{Ph_3C^-K^+}$ is present.

It thus appears that, in general, although the equilibrium basicity of this medium with respect to carbon acids is lowered, the "kinetic basicity" is enhanced when small amounts of alcohol are added. The catalysis by ROH has been observed for all base concentrations examined. At present, it is difficult to interpret our results in terms of the previous measurements of Ritchie.[8c] Large differences in concentrations may be responsible for profound effects in this system as in others.[8] Further results are discussed in the accompanying communication.[10] Finally, we wish to point out that for synthetic work involving proton removal, solutions of *t*-$\mathrm{BuO^-K^+}$ in DMSO can be as effective as or more effective than solutions of $\mathrm{CH_3SOCH_2^-K^+}$, and they are much easier to prepare.

Acknowledgment. We are grateful to the National Science Foundation (Grant GP 6736) and to the Petroleum Research Fund, administered by the American Chemical Society (Grant 2917-A4), for support of this research.

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[7] This double-resonance technique permits observation of slow rate processes by saturation at one site followed by chemical exchange.[8]

[8] J. I. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Am. Chem. Soc.*, **89**, 1728 (1967), and references cited therein.

[9] Double-resonance experiments were carried out with a Varian HA-100 spectrometer; we thank Dr. Lois J. Durham for her help with them.

[10] J. I. Brauman and N. J. Nelson, *J. Am. Chem. Soc.*, **90**, 491 (1968).

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Received November 13, 1967

The Effect of Alcohol on Proton Exchange Reactions in Dimethyl Sulfoxide. II. High Alcohol Concentrations

Sir:

In the accompanying communication[1] we reported the accelerating effect of small amounts of *t*-butyl alcohol (ROH) on the rate of proton removal from dimethyl sulfoxide (DMSO) and from triphenylmethane in the presence of $\mathrm{CH_3SOCH_2^-K^+}$. In this communication we report the effects of relatively large amounts of ROH on proton transfers of DMSO in the DMSO–ROH system.

At least three proton exchange reactions can occur in these solutions (eq 1–3). *We observe that even in solutions containing ~10% ROH, with 0.1 M base, appreciable proton exchange occurs between DMSO and* $\mathrm{CH_3SOCH_2^-}$ *(eq 2).*

$$\mathrm{ROH + RO^-K^+ \rightleftharpoons RO^-K^+ + ROH} \qquad (1)$$

$$\mathrm{DMSO + CH_3SOCH_2^-K^+ \rightleftharpoons CH_3SOCH_2^-K^+ + DMSO} \qquad (2)$$

$$\mathrm{DMSO + RO^-K^+ \rightleftharpoons CH_3SOCH_2^-K^+ + ROH} \qquad (3)$$

This follows directly from an analysis of the relative broadening of the peaks corresponding to the protons of DMSO and ROH. In these solutions it is possible to observe, by nmr, a peak corresponding to the hydroxylic proton of ROH. This peak is appreciably broadened in comparison with its width in the absence of base; the extent of broadening is highly dependent on ROH concentration, decreasing as ROH increases. The width of the OH peak can be associated with the lifetime of the proton on oxygen by use[2] of eq 4; eq 1 cannot contribute to this broadening

$$1/T_2' = (1/T_2) + (1/\tau_{\mathrm{ROH}}) \qquad (4)$$

since in eq 1 the chemical environment of the proton is unchanged. Presumably, then, the entire OH broadening is due to eq 3. The measured lifetime, τ_{ROH}, thus refers only to protons exchanged with DMSO. Given τ_{ROH} it is possible to determine $\tau_{\mathrm{DMSO\text{-}3}}$, the lifetime of a proton on DMSO due to eq 3, by considerations of detailed balancing (eq 5). It is, in addition, possible to determine the "total" lifetime

$$\tau_{\mathrm{DMSO\text{-}3}} = \tau_{\mathrm{ROH}} 6[\mathrm{DMSO}]/[\mathrm{ROH}] \qquad (5)$$

of a proton on DMSO, τ'_{DMSO}, by measuring the width of the ^{13}C satellite.[1,3] In these solutions, τ'_{DMSO} is clearly shorter than $\tau_{\mathrm{DMSO\text{-}3}}$, indicating that some protons on DMSO are being exchanged without the intervention of ROH. Qualitatively this is seen as follows. The OH broadening must be accompanied by a broadening of the ^{13}C satellite (proportional to the concentration of ROH and DMSO). In fact, the ^{13}C satellite is much broader than one would expect on the basis of OH broadening; the most likely pathway for the additional exchange is eq 2. The lifetime for this exchange, $\tau_{\mathrm{DMSO\text{-}2}}$, can be obtained by use of eq 6. In

$$1/\tau_{\mathrm{DMSO\text{-}2}} = (1/\tau'_{\mathrm{DMSO}}) - (1/\tau_{\mathrm{DMSO\text{-}3}}) \qquad (6)$$

Table I are summarized some typical results. It can

Table I. Lifetimes of Protons on DMSO and ROH

Base, *M*	[*t*-BuOH]/[base]	τ_{ROH}, sec	τ'_{DMSO}, sec	$\tau_{\mathrm{DMSO\text{-}3}}$, sec	$\tau_{\mathrm{DMSO\text{-}2}}$, sec
0.316	5.0	0.022	0.84	1.0[a]	5.9[a]
0.282	5.6	0.024	0.84	1.1[a]	3.6[a]
0.203	7.5	0.034	1.06	1.6	3.0
0.108	14.1	0.060	1.2	2.9	2.1

[a] Under these conditions, within experimental error, $\tau'_{\mathrm{DMSO}} \approx \tau_{\mathrm{DMSO\text{-}3}}$.

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[1] J. I. Brauman, N. J. Nelson, and D. C. Kahl, *J. Am. Chem. Soc.*, **90**, 490 (1968).

[2] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

[3] J. I. Brauman and N. J. Nelson, *J. Am. Chem. Soc.*, 88, 2332 (1966).

be seen that with increasing ROH concentration the exchange proceeds increasingly through $CH_3SOCH_2^-K^+$. Because we are unable to measure the relative concentrations of $CH_3SOCH_2^-K^+$ and RO^-K^+, we cannot assign rate constants for these reactions. The evidence is clear, however, that some $CH_3SOCH_2^-K^+$ must be present and reacting. This is also consistent with our observation that alkylations with $CH_3SOCH_2^-$ can be carried out almost instantaneously even in the presence of large amounts of alcohol.[4]

The results reported here are surprising in view of what has been assumed regarding the composition of solutions of DMSO–ROH–RO^-K^+.[5] It is possible that DMSO, behaving as a protic solvent, exerts a leveling effect similar to that of other solvents and that the apparent basicity of the solvent medium relative to "typical" carbon acids is a thermodynamic effect which involves ROH and $CH_3SOCH_2^-K^+$. Until now there has been no unambiguous way of determining the composition of the basic species undergoing reaction. It is clear, from our work as well as that of Ritchie,[6] that the properties of DMSO as a solvent for base-catalyzed reactions are significantly different from those expected of an "inert" solvent. As we have pointed out previously,[3] DMSO should not be characterized as aprotic, in spite of a continuing tendency for some workers to designate it in this way.[7] We emphasize that analyses of kinetic and thermodynamic basicities in DMSO must be approached with caution.

Acknowledgment. We are grateful to the National Science Foundation (Grant GP 6736) and to the Petroleum Research Fund, administered by the American Chemical Society (Grant 2917-A4), for support of this research.

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[4] See also A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964).

[5] See ref 1 for literature references.

[6] C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **86**, 4488 (1964); **89**, 1730, 2960 (1967).

[7] D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967).

[8] Stauffer Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

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Received November 13, 1967

The Electronic Multiplicity of Photolytically Generated Cyanonitrene

Sir:

We recently reported[1] that thermal fragmentation of cyanogen azide (N_3CN) in solution occurs with over-all conservation of spin to produce electronically excited singlet cyanonitrene (^1NCN) which inserts stereospecifically into tertiary C–H bonds. In addition, we indicated[2] that initially produced singlet NCN will, under certain conditions, undergo efficient spin-forbidden decay to its triplet ($^3\Sigma_g{}^-$) ground state[3-5] which reacts in a totally stereorandom fashion with tertiary C–H links. Similar conclusions concerning the electronic multiplicity of initially formed NCN and its spin-forbidden crossing to the ground state were also arrived at from experiments involving flash photolysis of N_3CN in the gas phase.[6] Recent work,[7] however, on the flash photolysis ot N_3CN in a solid nitrogen matrix appears to indicate that the photofragmentation of this molecule is not a simple process, as the multiplicity of initially produced NCN was found to be a function of the energy of the light employed. For example, it was observed that irradiation of N_3CN through quartz produces singlet ($^1\Delta_g$) NCN, whereas illumination through a Pyrex filter generates NCN exclusively in its $^3\Sigma_g{}^-$ ground state. To reconcile these results with the known ultraviolet spectrum of N_3CN[8] (λ_{max} 2750 (ϵ 103) and 2200 Å (ϵ 2157)) it was suggested[7] that, whereas decomposition of this molecule from the 2200-Å excited state occurs with conservation of spin, fragmentation from the lower energy state (2750 Å) violates the requirement of quantization of spin. Alternatively, the direct formation of $^3\Sigma_g{}^-$ NCN was viewed to occur with over-all conservation of spin on the condition that the 2750-Å band in the spectrum of N_3CN represents a singlet-to-triplet transition.[9]

Though both suggestions account for the facts, it is not clear why spin is not conserved in the fragmentation of the azide from a low-energy excited state or, if the 2750-Å band is indeed due to a spin-forbidden transition, why it should be as intense as it is. In an attempt to answer these questions satisfactorily we carried out the photolysis of N_3CN at a variety of wavelengths and determined the electronic multiplicity of the generated NCN by examining the stereochemical course of its insertion into the tertiary C–H bonds of 1,2-dimethylcyclohexane. Irradiations of solutions of N_3CN in the hydrocarbon were carried out at $\sim$15° with a 450-w "Hanovia" high-pressure lamp employing Vycor (absolute cutoff point at $\sim$2120 Å), Corex (absolute cutoff point at $\sim$2580 Å), and Pyrex (absolute cutoff point at $\sim$2800 Å) filters. As anticipated on the basis of the ultraviolet spectrum of N_3CN, nitrogen evolution was considerably slower on illumination through Pyrex than through Vycor or Corex.[10] Reduction of the resulting cyanamides to the corresponding amino and methylamino substrates and gas chromatographic analysis of these was accomplished in the manner described in earlier reports.[1,2] The results are collected in Table I.

The data collected in Table I clearly establish that photolytically generated NCN inserts into tertiary C–H

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[1] A. G. Anastassiou and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 3177 (1967).

[2] A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

[3] G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964).

[4] G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3735 (1965).

[5] E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).

[6] H. W. Kroto, *J. Chem. Phys.*, **44**, 831 (1966).

[7] L. J. Schoen, *ibid.*, **45**, 2773 (1966).

[8] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

[9] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **45**, 1387 (1966).

[10] Nitrogen evolution on irradiation of N_3CN through either Vycor or Corex occurred *ca.* six times faster than when the irradiation was carried out through Pyrex. This rate difference strongly suggests that fragmentation of N_3CN occurs from an electronically excited state rather than from a vibrationally excited ground state.