near 24,600 cm.$^{-1}$ ($\epsilon \sim$ 775 1./mole-cm.). No other maxima or shoulders indicative of other d–d bands were found, but the 8000-cm.$^{-1}$ band was broad and could possibly encompass unresolved components.

These spectra are attributed to tetrahedral, or mildly distorted tetrahedral, $CuCl_4{}^{2-}$ on the basis of a comparison of the position of the d–d band with the d–d band of crystalline Cs_2CuCl_4[5] at 9000 cm.$^{-1}$ and that of copper(II)-doped Cs_2ZnCl_4[5] at 8300 cm.$^{-1}$. The band energy shifts toward lower values with decreasing distortion of the $CuCl_4{}^{2-}$ complex, and presumably the $CuCl_4{}^{2-}$ complex in the melts is less distorted than in the crystals.

These results may be rationalized in terms of ligand field theory.[6] In the limit of no distortion from T_d symmetry, the 8000-cm.$^{-1}$ band of $CuCl_4{}^{2-}$ would be assigned to the $\Gamma_7(^2D_{5/2}) \to \Gamma_8(^2D_{3/2})$ transition with a Dq value of about 700 cm.$^{-1}$ when the spin–orbit coupling parameter is chosen to have the free-ion value of -830 cm.$^{-1}$. Only one other d–d band is expected for T_d symmetry, $\Gamma_7(^2D_{5/2}) \to \Gamma_8(^2D_{5/2})$. This band will occur far into the infrared region at about $-(3/2)\lambda - (3/20)\lambda^2/Dq$. The above tetrahedral Dq value of 700 cm.$^{-1}$ may be compared with the Dq for octahedral $CuCl_6{}^{4-}$ in copper(II)-doped $CsCdCl_3$.[7] The latter substance has a broad absorption at about 12,400 cm.$^{-1}$ which, in terms of octahedral symmetry, is reasonably assigned to the $\Gamma_8(^2D_{5/2}) \to \Gamma_7(^2D_{5/2}), \Gamma_8(^2D_{3/2})$ transitions with a Dq of -1250 cm.$^{-1}$. This gives $|Dq_{tet}/Dq_{oct}| = 0.56$ for chlorocopper(II) complexes. The corresponding ratio for chloronickel(II) complexes[8] is about 0.6. The $CuCl_4{}^{2-}$ complex observed in CsCl and Phosphon melts may be somewhat distorted from regular tetrahedral symmetry so that the above assignment and numerical value of the ligand field parameters have only an approximate significance. Karipides and Piper[9] have assigned the spectrum of Cs_2CuBr_4 in terms of subcubic symmetry species, but $CuCl_4{}^{2-}$ in melts is almost certainly much less distorted than $CuBr_4{}^{2-}$ in Cs_2CuBr_4.

The lowest energy charge-transfer band in crystalline Cs_2CuCl_4 is reported[2a] at about 24,000 cm.$^{-1}$, in agreement with the molten salt spectra. A similar band of $CuBr_4{}^{2-}$ has been assigned by Braterman[10] in a reasonable way to an electron jump from a nonbonding ligand orbital into a d-type orbital. Assignments of higher energy charge-transfer bands using Braterman's model are open to question, since he neglects electron jumps which originate in d-orbitals and terminate in antibonding orbitals.

Previous studies have been made of the spectrum of $CuCl_2$ dissolved in the LiCl–KCl eutectic melt[7,11,12] and it was proposed that this spectrum is that of tetrahedral $CuCl_4{}^{2-}$. However, the maximum of the d–d absorption was found at 9500 cm.$^{-1}$ so that if the tetrachloro complex is present in this system, it must be extremely distorted.

(5) W. E. Hatfield and T. S. Piper, to be published.
(6) A. D. Liehr, J. Phys. Chem., 64, 43 (1960).
(7) D. M. Gruen and R. L. McBeth, "Coordination Chemistry," Butterworth and Co., London, 1963, pp 23–47.
(8) Based on an analysis of the spectrum of Ni(II)-doped CsCdCl₃ in reference 7 and the Dq value for Ni(II)-doped Cs₂ZnCl₄ from H. A. Weakliem, J. Chem. Phys., 36, 2117 (1962).
(9) A. G. Karipides and T. S. Piper, Inorg. Chem., 1, 970 (1962).
(10) P. S. Braterman, ibid., 2, 448 (1963).
(11) G. Harrington and B. R. Sundheim, Ann. N. Y. Acad. Sci., 79, 950 (1960).
(12) D. M. Gruen and R. L. McBeth, Nature, 194, 468 (1962).
(13) Operated for the U. S. Atomic Energy Commission by Union Carbide Corp.

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Spin Exchange in Solutions of Potassium Naphthalenide

Sir:

We have studied the spin exchange interaction as a function of radical concentration and temperature in dilute solutions of potassium naphthalenide in tetrahydrofuran (THF) through observation of the breadths of hyperfine components in the electron spin resonance (e.s.r.) absorption spectrum. At relatively high concentrations of free radical and temperatures the line breadths vary very nearly linearly with radical concentration. In contrast to the case of $K_2NO(SO_3)_2$ dissolved in water,[1] this linear relationship extrapolates through the origin without application of a correction factor. It seems likely that the contributions of spin exchange and other factors to the line breadth are not simply additive in the naphthalenide–THF system. As for $K_2NO(SO_3)_2$ in water we observe that line shapes deviate from Lorentzian at low concentrations of radicals. The lower the temperature, the higher the concentration at which deviation from the Lorentzian shape is first noticed. At 0.39×10^{-3} M the lines observed are nearly gaussian even at room temperature.

The second-order rate constants derived from the slopes of the line width vs. concentration plots vary from 2.8×10^9 1. mole^{-1} sec.$^{-1}$ at $20°$ to 1.1×10^9 1. mole^{-1} sec.$^{-1}$ at $-60°$. The rate constant varies linearly with kT/η, where η is the viscosity of the solvent above $-30°$, and the plot extrapolates through the origin within experimental uncertainty. This indicates that exchange takes place at every appropriate collision.[2] Thus, the rate constants given above are approximately half the rate constants for bimolecular encounters between the free-radical molecules.

If spin exchange is the dominant mechanism of line broadening, different hyperfine lines should broaden at different rates as in the case of electron exchange between radical ion and parent hydrocarbons.[3] A sensitive method of detecting line breadth changes within a spectrum is to compare the amplitudes of the derivative curves of the lines. A variation in line breadth shows up as a deviation of the ratio of amplitudes from that calculated on the basis of equal breadths.

A comparison between experimental and theoretical amplitude ratios is given in Table I for a 1.35×10^{-3} M solution at 40 and $0°$. The agreement between experimental and theoretical values is seen to be excellent at $40°$ while at $0°$ considerable deviation is noted. We interpret this to mean that spin exchange almost completely determines the line width at $40°$, but only contributes to the breadth at $0°$ in this solution.

TABLE I

DERIVATIVE CURVE AMPLITUDE RATIOS[a]

2	9[b]	11.77[c]	11.8[d]	10.3[e]
3	6[b]	7.75[c]	7.87[d]	6.77[e]
11	1.5[b]	1.67[c]	1.65[d]	1.53[e]

[a] The ratios are of the amplitude of the line 13 in the naphthalenide spectrum to that of the line whose number is given in the first column. The lines are numbered in succession from high field to low field. [b] Ratios calculated on the basis of equal line widths. [c] Ratios calculated on the basis that spin exchange determines the line widths completely. [d] Experimental ratios at $40°$ for a 1.35×10^{-3} M solution. [e] Same as footnote d except at $0°$

(1) M. T. Jones, J. Chem. Phys., 38, 2892 (1963).
(2) (a) J. D. Currin, Phys. Rev., 126, 1995 (1962); (b) D. Kivelson, J. Chem. Phys., 33, 1094 (1960); (c) G. E. Pake and T. R. Tuttle, Jr., Phys. Rev. Letters, 3. 423 (1959).
(3) P. J. Zandstra and S. I. Weissman, J. Chem. Phys., 35, 757 (1961).

While our results confirm the theory within the experimental error, the results of Powles and Mosley[4] on solutions of potassium biphenylide are only in rough agreement with the theoretical predictions. The exchange frequency they estimate at $-62°$ in tetrahydrofuran gives a second-order rate constant for spin exchange about ten times larger than our value at $-60°$ in the same solvent. Although the two systems differ in the anion, this cannot account for such a large discrepancy. It seems probable that their solutions of potassium biphenylide contained substantial amounts of unreduced hydrocarbon. Such solutions would give apparently high values for exchange rates because of the contribution of electron exchange between free radical and parent hydrocarbon.

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(4) J. G. Powles and M. H. Mosley, *Proc. Phys. Soc.* (London), **78**, 370 (1961).

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Derivatives of 3H-Azepine[1]

Sir:

Despite the fact that the introduction of hetero atoms into the tropylium ion π-lattice is predicted to lower the energy of the resulting species and render it highly susceptible to oxidation,[2] effort in many laboratories continues to be directed to eventual syntheses of azepine (I, X = NH), oxepine (I, X = O), and thiepine (I, X = S).

Recent reports in the area of azepine chemistry[3,4] prompt us to report a ready synthesis of derivatives of 3H-azepine.

A remarkable ring expansion of 2,6-dialkyl- and 2,4,6-trialkylphenols to 1,3-dihydro-2H-azepin-2-ones was recently reported from this Laboratory.[5] We have now found that the dihydroazepinones react readily with triethyloxonium fluoroborate[6] to afford 2-ethoxy-3H-azepines. For example, reaction of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (II) with triethyloxonium fluoroborate in methylene chloride solution at room temperature gave a very good yield of 2-ethoxy-3,5,7-trimethyl-3H-azepine (IIIa). The structure of IIIa follows from its analysis,[7] its infrared spectrum which shows the absence of the amide absorption patterns associated with II, and its ultraviolet [λ_{max}^{EtOH} 257 mμ (6300)] and n.m.r. spectra.[8] The n.m.r. spec-

(1) Dihydroazepinone Chemistry. VII. For paper VI of this series, see L. A. Paquette, *J. Am. Chem. Soc.*, in press.

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 280–281.

(3) R. Huisgen and M. Appl [*Ber.*, **91**, 12 (1958)] have postulated the aminoazepine (i) as an intermediate in the decomposition of phenyl azide in aniline; if formed, i tautomerizes rapidly to the more stable 7H-azepine (ii).
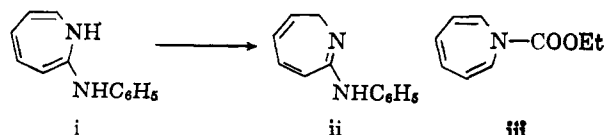

(4) K. Hafner and C. Koenig [*Angew. Chem.*, **75**, 89 (1963)] and W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr. [*J. Am. Chem. Soc.*, **85**, 1200 (1963)] have shown that generation of carbethoxynitrene in the presence of benzene affords N-carbethoxyazepine (iii), which readily isomerizes to phenylurethan.

(5) L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962); **85**, 3288 (1963).

(6) H. Meerwein, *et al.*, *J. prakt. chem.*, **147**, 257 (1937); **154**, 83 (1939).

(7) All new compounds reported herein have satisfactory carbon, hydrogen, and nitrogen elemental analyses.
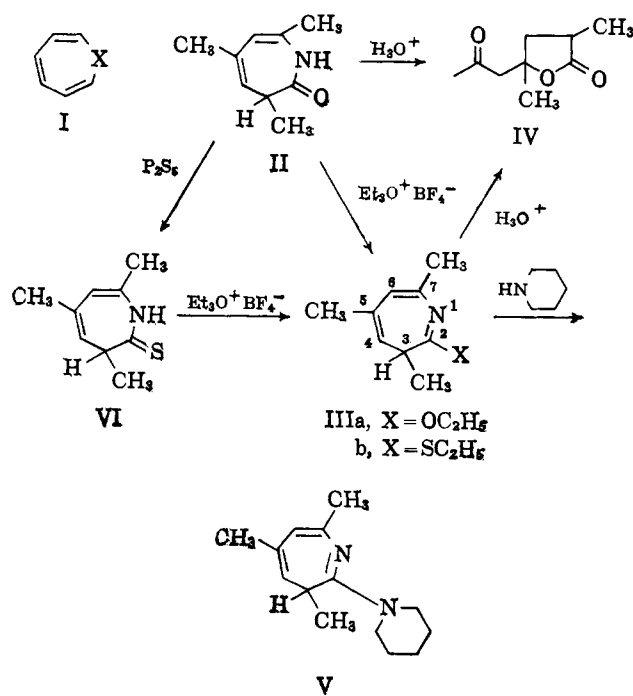
trum is in full agreement with the proposed structure (IIIa); a broad singlet at 345 c.p.s. was assigned to the proton at position 6, a doublet centered at 282 c.p.s. ($J = 5$ c.p.s.) to the proton at position 4, and a 5-line pattern centered at approximately 120 c.p.s.[9] to the ring proton at 3. In addition, the absorption peaks of the various methyl groups were located at 123 (singlet, 7-methyl), at 109 (triplet, $J = 1.5$ c.p.s., 5-methyl), at 82.5 (doublet, $J = 7$ c.p.s., 3-methyl), and at 73 c.p.s. (triplet, $J = 7.5$ c.p.s., CH_3 of the ethoxy moiety). The interesting aspect of this spectrum was the appearance of the methylene portion of the ethoxy group as an AB system, *indicating restricted rotation of this grouping*. This complex system of four mutually overlapping quartets was centered at 245 c.p.s.

Acid hydrolysis of IIIa proceeded rapidly to give the keto-lactone (IV), identical in all respects with the product arising from acid hydrolysis of II.[5] Therefore, a rearrangement of the carbon skeleton of II can be precluded in the triethyloxonium fluoroborate reaction.

The 3H-azepine (IIIa) is a remarkably stable substance under normal conditions and has been stored for prolonged periods at room temperature without apparent change. In addition, IIIa surprisingly can be recovered in excellent yield after heating with excess methyl iodide at $100°$ for 7 hr. in a sealed tube. Prolonged heating (5 days) of IIIa in refluxing excess piperidine afforded 58% recovery of IIIa and a 72% yield (based on recovered 3H-azepine) of 2-piperidino-3,5,7-trimethyl-3H-azepine (V), characterized as its perchlorate salt, m.p. $156–157°$.[7] Thus, *IIIa is capable of nucleophilic substitution*.

We have also found that II could be converted to its thio analog, 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-thione (VI), m.p. $136.5–137°$,[7] in good yield with phosphorus pentasulfide in refluxing pyridine. Similar reaction of VI with triethyloxonium fluoroborate gave a good yield of 2-ethylthio-3,5,7-trimethyl-3H-azepine (IIIb), b.p. $76°$ (0.25 mm.).[7] The n.m.r. spectrum of this material was very similar to that of IIIa, with the

(8) All n.m.r. spectra herein discussed were obtained on a Varian A-60 spectrometer in dilute deuteriochloroform solutions, using tetramethylsilane as internal reference (TMS = 0).

(9) This absorption pattern is complicated because of the overlapping absorptions of the methyl groups at positions 5 and 7.