generacy of the hyperfine components in the spectrum of TAA^{+2} prevents a quantitative interpretation of the line-width variations.[10] Since the spin density at the nitrogen nucleus is high (Table I), one can predict, however, that relaxation contributions due to the ^{14}N nucleus will be considerably larger than those due to the protons (*cf.* ref 12). The differences in line widths between the three groups of hyperfine components, therefore, can be attributed primarily to terms linear and quadratic in the ^{14}N nuclear quantum number

$$T_2^{-1} = KM_N^2 + LM_N$$

where K and L are constants[10,12] and T_2^{-1} is the contribution to the line width. The second right-hand term in this expression can be used, together with the observation that the high-field components are broader than the corresponding low-field components, to derive the sign of the ^{14}N hfs constant.[12–14] Following the arguments which have been presented previously,[12,14] one can show that L, a constant containing the g-tensor components and the electron spin–^{14}N nuclear spin dipolar interaction component along the trigonal axis of the radical, must be negative. The group with $M_N = -1$ will, therefore, be broader than the group for which $M_N = +1$, so that our experimental finding leads to the conclusion that the ^{14}N hfs constant must be positive. This is in agreement with the sign derived with the help of the modified Karplus–Fraenkel formula[15] relating the ^{14}N hfsc to the spin densities on ^{14}N and its neighboring carbon atoms.[16,17]

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Vibrational Bands of Alkali Metal Salts in Dimethyl Sulfoxide

Sir:

Recently Edgell and co-workers have reported[1] their observation on the vibrational spectra of Li$^+$, Na$^+$, and K$^+$ salts of Co(CO)$_4^-$ and Mn(CO)$_5^-$ anions in tetrahydrofuran solutions. The three salts of the first anion show infrared bands at 407, 190, and 150 cm^{-1}, respectively, while the corresponding bands of the Mn(CO)$_5^-$ salts are shifted to higher frequencies by 20–30 cm^{-1}.

We wish to report our observation of the spectra of ammonium and alkali metal salts in dimethyl sulfoxide solutions. The data are given in Table I. It is seen that in our case the absorption band is essentially independent of the nature and the mass of the anion and, therefore, should be due to the interaction of the cation with the solvent molecules.

Table I. Absorption Band of Alkali Salts in Dimethyl Sulfoxide

Compound	Concn, *M*	ν_{max}, cm^{-1}
LiCl[a]	0.4	429 ± 2
LiBr	0.4	429 ± 2
LiI	0.9	429 ± 2
LiNO$_3$	0.4	429 ± 2
LiClO$_4$	0.5	429 ± 2
NH$_4$Cl	Satd	214 ± 5
NH$_4$Br	0.4	214 ± 4
NH$_4$I	0.7	214 ± 4
NH$_4$NO$_3$	0.4	214 ± 4
NH$_4$ClO$_4$	0.5	214 ± 4
NH$_4$SCN	0.5	214 ± 4
NaCl	Satd	199 ± 5
NaBr	Satd	199 ± 3
NaI	1.0	198 ± 3
NaNO$_3$	1.0	206 ± 3
NaSCN	1.0	200 ± 3
NaPh$_4$B	0.26	198 ± 3
NaNO$_3$	0.60 (in 2:1 C$_6$H$_6$–DMSO mixt)	205 ± 3
KBr	0.5	153 ± 3
KI	1.0	153 ± 3
KNO$_3$	1.0	154 ± 3
KSCN	1.0	153 ± 3
RbI	3.0	129 ± 4
RbNO$_3$	0.5	123 ± 5
CsI	Satd (~1.5 *M*)	118 ± 6

[a] The Li$^+$ bands have a shoulder at ~414 ± 2 cm^{-1}.

Table II. Calculated and Observed Band Frequencies

Cation	ν_{calcd}, cm^{-1}	ν_{obsd}, cm^{-1}
Li$^+$	335	429
NH$_4^+$	221	214
Na$^+$	...	200
K$^+$	165	153
Rb$^+$	132	125
Cs$^+$	120	118

We made an admittedly very crude assumption that the observed absorption bands are due to a cation–solvent molecule vibration and that the force constants did not change with the change in the cation. Taking the Na$^+$ band as the standard, we calculated the frequencies of other bands. The results are shown in Table II.

It is, of course, quite evident that the force constants would vary with the nature of the cation and that the alkali metal ions are solvated by several molecules of DMSO. Nevertheless the trends are consistent and seem to indicate the ion–solvent interaction. The large disagreement in the case of lithium salts is to be expected in view of the known coordinating ability of the lithium ion. Further studies of the above and similar systems are now in progress.

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A Peroxide Fragmentation Reaction

Sir:

Tertiary dialkyl peroxides are normally insensitive to base.[1] We wish to report a unique decomposition of a tertiary peroxide in a basic medium.

When 2-*t*-butylperoxy-2-methylpropionic acid (I) was treated with triethylamine in chlorobenzene at

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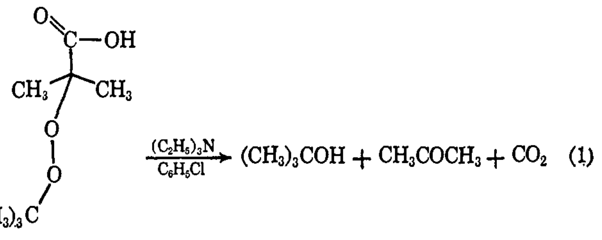
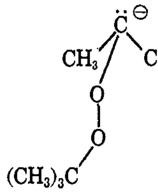


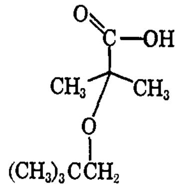
I

25°, acetone and *t*-butyl alcohol were produced in quantitative yield along with carbon dioxide. Acetone and *t*-butyl alcohol were identified by comparison of gas–liquid partition chromatography (glpc) retention times with authentic samples. In addition, the infrared spectra of fractions collected by glpc were identical with those of acetone and *t*-butyl alcohol. The structure of I was established by its infrared (carboxyl group: 2570, 2670, 1730 cm^{-1}; peroxide group, tentative: 875, 1175 cm^{-1}) and nmr (α-methyl protons: 1.45 ppm, singlet, area = 6; *t*-butyl protons: 1.23 ppm, singlet, area = 9; carboxyl proton: 11.6 ppm, singlet, area = 1) spectra along with analytical data. *Anal.* Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.86; H, 9.34. Acid I was prepared by the following synthetic sequence: isobutylenechlorohydrin[2] was converted to isobutylene oxide;[3] the oxide was treated with *t*-butyl hydroperoxide in the presence of acid to give 2-methyl-2-*t*-butylperoxy-1-propanol; finally acid I was obtained by chromic acid oxidation of the alcohol. Details of the preparation of I will be reported later.

The closest analogy to the decarboxylative fragmentation reaction (1) is found in the fragmentation reactions of β-halo acids.[4] Data have been presented for two types of fragmentation mechanisms for the β-halo acids: one, a concerted elimination of bromide ion and carbon dioxide, and the other, a two-step process where ionization of the carbon–bromine bond occurs initially, followed by loss of carbon dioxide. The analogous mechanisms may be considered for I where *t*-butoxide is the leaving group rather than bromide. In addition, a third mechanism is possible where carbon dioxide is lost to give II. Subsequent reaction of II will give *t*-butoxide and acetone. Of these three mechanisms, the concerted process from the amine salt of I is most likely. Unassisted heterolytic or homolytic rupture of the peroxide bond at 25° will be insignificant. For example, di-*t*-butyl peroxide has a half-life of 239 hr at 100° in benzene.[5]



II



III

Kinetic data are inconsistent with a two-step mechanism to give II as an intermediate. At 25° in chlorobenzene, the triethylamine salt of I has a half-life of about 25 min. In contrast, 2-methyl-2-neopentoxypropionic acid III is inert under identical conditions. The rates of decarboxylation of acids I or III to a carbanion intermediate should not differ greatly.

The structure of III was established by its infrared (carboxyl group: 2560, 2670, 1710 cm^{-1}; ether group: 1078, 1175 cm^{-1}) and nmr (α-methyl protons: 1.43 ppm, singlet, area = 6; *t*-butyl protons: 0.91 ppm, singlet, area = 9; methylene protons: 3.06 ppm, singlet, area = 2; carboxyl proton: 12.0 ppm, singlet, area = 1) spectra along with analysis of the methyl ester of III. *Anal.* Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.70. Found: C, 63.48; H, 11.07. Acid III was prepared by chromic acid oxidation of 2-methyl-2-neopentoxy-1-propanol. This alcohol was obtained from the acid-catalyzed reaction of isobutylene oxide[3] and neopentyl alcohol. The details of the synthesis will be presented later.

The 1,2-elimination reaction of peroxides with base has been reported.[6] Thus, benzyl *t*-butyl peroxide undergoes reaction with base to produce benzaldehyde and *t*-butyl alcohol.[6a] Similarly, 1-phenylethyl *t*-butyl peroxide gives acetophenone and *t*-butyl alcohol.[6b] Ionic rupture of the peroxide bond according to fragmentation reaction 1 finds analogy in these 1,2-elimination reactions.

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A Novel Type of Valence Tautomerism in Organometallic Complexes

Sir:

The occurrence of intramolecular rearrangements in organometallic complexes is well documented. The species which display the phenomenon largely fall into one of two categories. The first involves complexes in which a σ-bonded metal–carbon linkage is broken and re-formed in the rearrangement as in allylmagnesium systems and various σ-cyclopentadienyl–metal complexes.[1] The second class involves rearrangement of π-type complexes in which a metal atom is attached to three or more carbon atoms of a conjugated framework of sp^2 carbon atoms, most commonly fully conjugated cyclic systems; examples of this latter type include the valence tautomerism exhibited by cyclooctatetraene–$Fe(CO)_3$ and $-Fe_2(CO)_6$ complexes and cycloheptatrienyl–metal complexes.[2] We wish now to report a novel

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