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Nuclear Magnetic Resonance Studies of the Di-, Tri-, and Tetramethylammonium Ions Oriented in Middle Nematic Soap Phases

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Abstract: Preparative methods are described for the production of middle nematic soap phases from dimethyl-, trimethyl-, and tetramethylammonium decyl sulfates. The nuclear magnetic resonance (nmr) spectra of the oriented ions have been investigated. In the case of dimethylammonium ion, both the N-14 and N-15 containing ions give useful structural information and a set of reasonable geometric parameters have been obtained from minimum assumptions. The spectra depend on the pH of the water used to prepare the phases and since degrees of orientation do not vary widely in the phases prepared, this permits the analysis to proceed in stages. The neutral phase yields an A_3A_3' spectrum, the acidified phase an $A_3A_3'B_2$ spectrum, while the N-15 labeled ion in an acidified phase provides an $A_3A_3'B_2M$ spectrum. Distances of closest approach of methyl protons indicate some hindered rotation on purely steric grounds. The orientation of the trimethylammonium ion in acidified middle phases gives an extremely complex $A_3A_3'A_3''B$ spin system which, because of overlapping transitions, has not been analyzed. No structural information is possible from the analyzed $A_3A_3'A_3''$ spectrum in neutral phases. There is some evidence from the increase in line width of the apparently single transition that the tetramethylammonium ion is oriented in the middle nematic phase prepared.

Lyotropic nematic middle phases[2] have been used since 1967[3] as orienting media for small molecules. Recent work from this laboratory[4,5] has shown that these phases can be generalized in practice to include complex ion detergents. Simple monatomic species such as alkali metal ions are ordered by the superstructure of the nematic phase and exhibit first-order quadrupole splittings in their nuclear magnetic resonance spectra (nmr).[6] Both cationic and anionic[4,5] detergents of complex ions can be prepared as components of middle phases, which then manifest the ordering of the complex ion by typical nmr spectra, which contain information on intra-ionic dipole–dipole coupling.[7–9] These spectra provide an experimental determination of the internuclear distance ratios in the same manner as the spectra from oriented molecules in thermotropic nematic phases.[7–9] We have recently shown that both small cations and anions are ordered in the electrical double layer of a cationic detergent phase.[10–12]

The study of these methylammonium ions with emphasis on the dimethylammonium ion correlates well with several other studies of ions. The structural characteristics of dimethyltin, methylammonium, acetate, methylmercury, and trimethyllead ions have also been investigated.[11,13–15]

Experimental Section

(a) **Preparation of Compounds.** Di- and trimethylammonium decyl sulfates were prepared by two methods from the hydrochlorides and sodium decyl sulfate.

Method I. Dowex 50 exchange resin (25 ml) was washed with 20 ml of 1 *N* HCl to convert it into the acid form and then washed with distilled water until the effluent was neutral to pH paper.

Aqueous solutions of the hydrochlorides (1 gm/50 ml) were passed slowly through the exchange column until the effluent had the same pH as the original solutions. The column was then further washed with distilled water (100 ml) and subsequently with a solution of 5 g of sodium decyl sulfate in 30 ml of water. The fraction which was slowly emitted from the column at this point was com-

Table I. Typical Compositions of Middle Nematic Phases Prepared from Dimethylammonium Decyl Sulfate (DMADS) and Trimethylammonium Decyl Sulfate (TMADS)[a]

Component	Weight, mg	Wt %
Phase I		
DMADS (N-15)	358	39.4
Decanol	42	4.6
Sodium sulfate	61	6.7
H_2O (pH ~1.5)	447	49.3
Phase II		
TMADS	568	48.0
Decanol	68	5.7
Sodium sulfate	62	5.2
D_2O	485	41.1
Phase III		
NaDS	424	40.4
Decanol	57	5.4
TeMA sulfate	51	4.9
D_2O	518	49.3

[a] Phase I was the phase used to orient the N-15 substituted dimethylammonium ion. Water was acidified with sulfuric acid in phase I to slow down proton exchange of the NH_2^+ protons. The abbreviation NaDS corresponds to sodium decyl sulfate and TeMA to tetramethylammonium. Many phases were prepared during this study and no particular difficulty was encountered.[4,5]
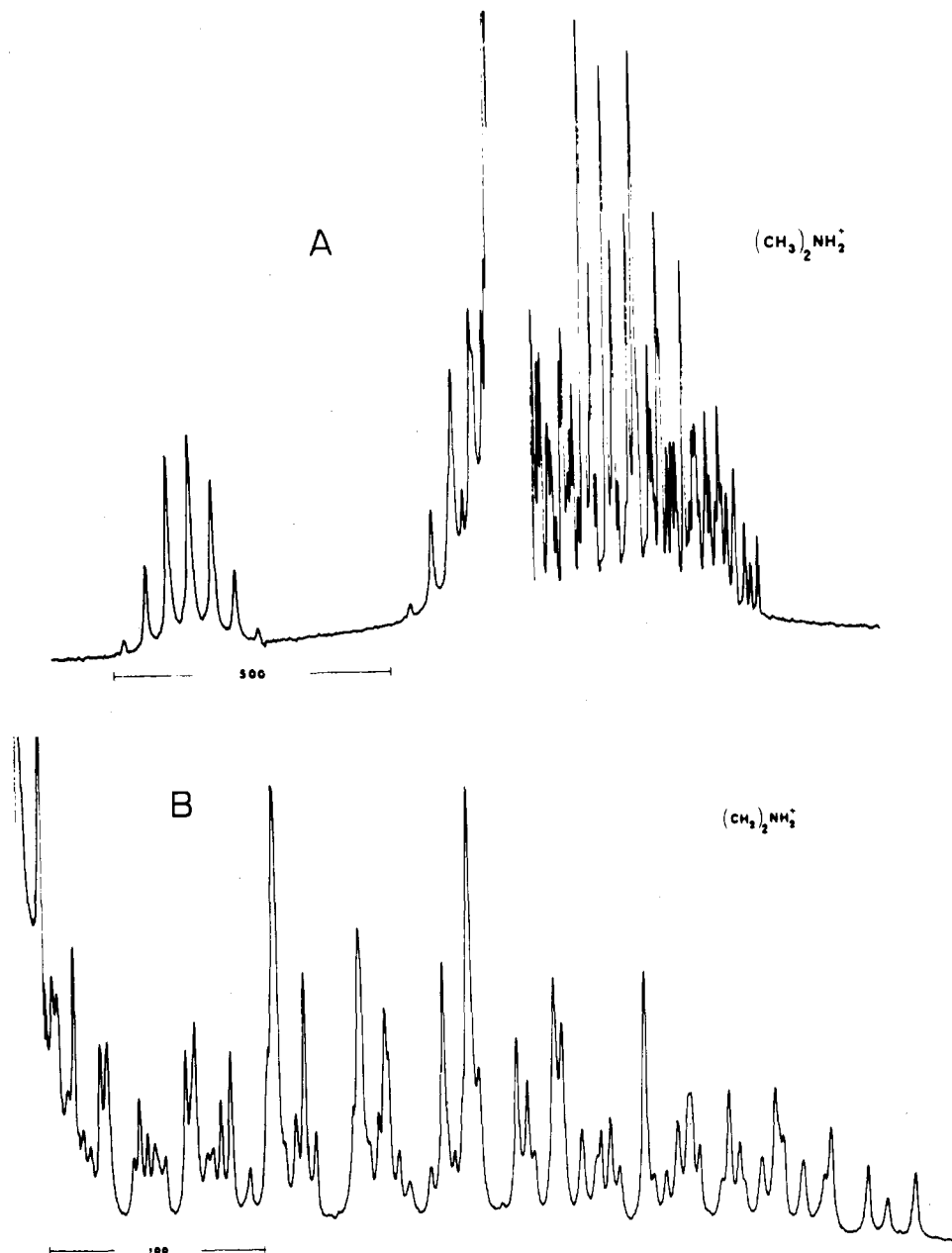
Figure 1. (A) Spectrum of the oriented dimethylammonium ion at 100 MHz. The calibration scale is 500 Hz. (B) Expanded spectrum of the methyl proton spectrum of the oriented dimethylammonium ion. The calibration scale is 100 Hz. Both spectra refer to ions with isotopes in natural abundances. The N-14 spin 1 is decoupled by rapid longitudinal relaxation with a dominant nuclear quadrupole mechanism.

bined with a 40-ml fraction of wash water then evaporated to dryness on a rotary evaporator. The products were recrystallized from petroleum ether to give a quantitative yield.

Method II. The N-15 (90% enriched) dimethylammonium chloride (Merck Sharp and Dohme) requires a more economical use of the labeled salts than method I sometimes allows. Dimethylammonium chloride (0.5 g) was added to 1.7 g of sodium decyl sulfate in 30 ml of chloroform. Water (1 ml) was then added to the mixture. The solution was refluxed until no crystals of sodium decyl sulfate remained; then the water was removed by codistillation with chloroform. The sodium chloride which forms is precipitated. The solution was filtered and if cloudy treated with carbon then refiltered through celite. The solution was finally evaporated and the product recrystallized from petroleum ether (30–60°). The yields were quantitative.

Compositions of nematic phases used in this study are listed in Table I. Proton magnetic resonance spectra were recorded from a Varian HA-100 spectrometer, with sample spinning at a probe temperature 31.1 ± 0.1°. Calibration was achieved by the difference frequency from the lock signal (water) rather than by reliance on chart paper calibration.

Results

(a) Dimethylammonium Ion. The spectra of the oriented dimethylammonium ion depends on the pH of the water used to prepare the middle nematic phase. A spectrum of the oriented ion in a nonacidified D_2O medium was presented in a previous communication.[4b] In Figure 1 the spectrum of oriented dimethylammonium ion without N-15 enrichment is presented for an acidified phase. In A of Figure 1 the complete spectrum is reproduced. The large peak which exceeds the height of the recorder is that of water in the phase. To the high field of water appears the almost symmetric spectrum of the six methyl protons while at low field is one-half of the spectrum of the NH_2^+ protons. The upper half of this doubleted septet lies partly under the water peak but the lower field transitions of the upper septet are clearly visible. The appearance of an $A_3A_3'B_2$ is easily identifiable in the spectrum. In B of Figure 1 the high field methyl spectrum is expanded to show the detailed fine structure.

Table II. Spectral Analyses (Hz) for the Oriented Dimethylammonium (N-15 Enriched) and Trimethylammonium Ions[a]

| | | $-(CH_3)_2{}^{15}NH_2{}^+-$ | | $(CH_3)_3{}^{14}NH^+$ |
	Isotropic		Anisotropic	Anisotropic
$J_{^{15}NH}$	-76.53	$D_{^{15}NH}$	111.01	
$J_{^{15}N-C-H}$	0.8	$D_{^{15}NCH_3}$	-8.91	
J_{HNCH}	5.66	D_{HNCH}	39.17	
		D_{HCH}	-112.75	D_{HCH} -72.80
		D_{HNH}	-391.04	
		$D_{H_3CNCH_3}$	49.31	$D_{H_3CNH_3}$ $*30.89$
		$J_{H_3CNCH_3}$	-0.01	$J_{H_3CNCH_3}$ $*0.28$
δ	515.3	δ	505.8	
RMS	0.05	RMS	0.47	RMS 0.50

[a] Column 1 refers to analysis of the isotropic acidified aqueous ion. The scalar couplings are used in the analysis of the anisotropic spectrum. "δ" is the internal chemical shift between methyl and $NH_2{}^+$ protons. RMS errors in fitting the selected transitions are placed at the foot of each column. All parameters measured in Hertz.

The spectrum of the 90% enriched N-15 dimethylammonium ion is a more complex $A_3A_3'B_2X$ spectrum with at least 330 observable transitions, neglecting those of low intensity. The two subspectra derived from the N-15 spin can be clearly seen for the $N^{15}H_2{}^+$ protons. Analysis proceeds in stages from the oriented nonacidified dimethylammonium ion which gives a A_3A_3' spectrum to the acidified dimethylammonium $A_3A_3'B_2$ spectrum then to the acidified dimethylammonium N-15 enriched compound which gives the $A_3A_3'B_2X$ spectrum. Orientations of these ions in different phases are not greatly different and initial estimates of chemical shifts can be derived from aqueous isotropic solutions. The final analysis of the oriented N-15 enriched methylammonium ion was achieved by selecting 177 transitions, which on final iteration were fitted with a root mean square (RMS) error of 0.47 Hz. The scalar couplings were derived from spectra of isotropic acidified aqueous solutions. The $A_3A_3'B_2X$ spectrum is quite close to $A_3A_3'M_2X$ because of the large chemical shift between nitrogen and methyl protons. A modified UEA computer program was used in the spectral analysis.[16] Dipole-dipole and scalar couplings are listed in Table II.

(b) **Trimethylammonium Ion.** In a phase prepared with water of pH ~7 the NH^+ proton is exchanging rapidly and the spectrum of the oriented ion $A_3A_3'A_3''$ is determined by three parameters $D_{H_3CNCH_3}$, D_{H-C-H}, and $J_{H_3CNCH_3}$ with no internal chemical shift. In acidified phases the 10 spin $A_3A_3'A_3''X$ spectrum becomes extremely complex and very few single transitions are observable. The analysis of the 9 spin spectrum for a typical anisotropic phase is given in Table II. Of some note is the observation of line width and position anomalies in the $A_3A_3'A''$ spectrum. These are reproducible on two spectrometers of different manufacture and do not depend on the particular phase prepared. The high field half of the theoretically symmetric spectrum is broadened on the order of 0.5 Hz more than the low field half and some systematic position anomalies of this order also occur. The overall RMS error on final iteration is not greatly affected. Eighty transitions were measured on each side of the very strong central transition. A considerable number of near degeneracies occur in line positions and this might partly explain position anomalies. The analysis was simplified by selecting five identifiable transitions which can be expressed analytically in terms of $D = D_{H_3CNCH_3}$ and $D' = D_{HCH}$. The transitions are: $-3D' = \nu_1$ (30), $-\frac{3}{2}D' = \nu_2$ (24), $\frac{3}{2}D = \nu_3$ (36), $(-\frac{3}{2}D' - \frac{3}{2}D') = \nu_4$ (9), and $(+\frac{3}{2}D - 3_5D') = \nu_5$ (3). Relative intensities of the transitions are given in parentheses after the frequencies

and these transitions include some of the most intense lines in the spectrum. From approximate values of D and D' the final iterative fitting to 28 of the 80 transitions was made, including an iteration on $J_{H_3CNCH_3}$. A good analysis of the $A_3A_3'A_3''X$ spectrum in the acidified phase was not possible because of its complexity. A solvent which leads to a higher degree of orientation is required so that fewer overlapping transitions will occur.

(c) **Tetramethylammonium Ion.** The spectrum of the oriented tetramethylammonium ion is of some interest because of our recent studies of ordered tetrahedral ions.[10,11,13] Some line broadening is observed but no fine structure can be resolved. A higher ordering solvent or observation of the deuterium spectrum of the partially or totally deuterated ion is required. Methanol in the same phase is ordered as manifested by the usual high resolution 1:2:1 triplet.

Discussion

Some estimates of the degrees of orientation of three Cartesian axes fixed within the ion can be made by assuming reasonable internuclear distances.[13] The chosen axes are the bisector of the HNH angle as y axis, the nitrogen nucleus as origin, the x axis perpendicular to the HNH plane, and the z axis perpendicular to the CNC plane. The angles and distances required are denoted in Figure 2. To obtain trial values of S_{zz}, the degree of orientation of the molecule fixed z axis, the $r_{HNH} = r_{12}$ distance in the $NH_2{}^+$ group is assumed to be 1.676 Å. Using the tabulated value $D_{12} = D_{HNH} = -391.04$ Hz, S_{zz} becomes 7.666×10^{-3}. Now assuming further that $r_{NH} = r_{32} = 1.034$ Å, the degree of orientation of the NH axis becomes 5.043×10^{-3} from the tabulated value $D_{23} = D_{^{15}NH} = 111.01$ Hz. These distances were estimated from our earlier study of the methylammonium ion[13] and provide the angles $\phi_{yy} = 54.14°$ and $\phi_{zz} = 35.86°$ which are preliminary assignments for calculating S_{yy} from the expression

$$S_{NH} = \cos^2 \phi_{zz} S_{zz} + \cos^2 \phi_{yy} S_{yy} \tag{1}$$

$S_{yy} = 6.97 \times 10^{-6}$. This value is a factor of 10^{-3} smaller than S_{xx} and S_{zz}. Since experimental errors in S_{xx} and S_{yy} have the same magnitude as S_{yy} it seems reasonable to obtain a feel for the effect of setting this value to zero by recalculating the ratio r_{12}/r_{23}. Expressing now the internuclear distance ratio

$$(r_{12}/r_{23})^2 = 4 \cos^2 \phi_{zz} \tag{2}$$

and deriving $D_{^{15}NH}$ in terms of S_{zz} we have

$$D_{NH} = \frac{C\gamma_N}{4r_{23}{}^3} \left(\frac{r_{12}}{r_{23}}\right)^2 S_{zz} \tag{3}$$

The constant C is derived of nuclear constants, which are common to expressions of this type.[7] D_{HNH} is given by

$$D_{HNH} = \frac{C\gamma_H}{r_{12}{}^3} S_{zz} \tag{4}$$

The ratio of (3) and (4) gives

$$\frac{D_{NH}}{D_{HNH}} = \frac{\gamma_N}{\gamma_H} \frac{1}{4} \left(\frac{r_{12}}{r_{23}}\right)^5 \tag{5}$$

From the values of the D's in Table II

$$r_{12}/r_{23} = 1.6213 \pm 0.0004 \tag{6}$$

If $r_{32} = 1.034$ Å (assumed) then $r_{12} = 1.6765 \pm 0.0003$ Å. This value is within 5×10^{-4} Å of our previous value for r_{12} (1.676 Å). Corrections of this magnitude are of dubious value. In the discussion which follows S_{yy} will be assumed to be zero. This simplifies the computation of the internuclear distance ratio leading to (6) which gives an angle $2\phi_{yy} = 108.32 \pm 0.03°$. In the methylammonium ion this angle

is 108.29°. The setting of S_{yy} to zero gives a slightly corrected value of $S_{zz} = 7.673 \times 10^{-3}$.

The degree of orientation of the C_3 axis of the N-methyl groups can be estimated by assuming an angle ϕ_{xx}. A recent X-ray diffraction study[17] of dimethylammonium chloride by Lindgren and Olovsson gives 113 ± 0.8° for the NCN angle. Thus ϕ_{xx} is 33.5°. From the result that $S_{yy} = 0$, S_{xx} is -7.673×10^{-3} since the sum $\Sigma S_{ii} = 0$. S_{C_3}, the degree of orientation of the local C_3 axis of the CH_3N moiety, is computed in a similar manner to (1) to give 5.336×10^{-3}. Relating $D_{HCH} = 112.75$ Hz to r_{HCH} by using the degree of orientation of the local C_3 axis S_{C_3}[7] a distance $r_{HCH} = 1.7844$ Å is obtained. If $r_{CH} = 1.096$ Å then the angle HCH = 108.99°. The corresponding angle in the methylammonium ion has been determined to be 110.12° [13] from a study of the nmr spectrum of the oriented ion. Such a discrepancy between the two ions is unlikely and this reflects back to the assumption regarding the CNC angle taken from the X-ray study.[17]

It is possible to utilize the local C_{3v} symmetry of the CH_3N moiety directly and avoid this assumption regarding the CNC angle. Unfortunately, unlike the previous investigation of the methylammonium ion, the C-13 enriched compound was not available to us, but the methodology follows that of this prior study.[13] The appropriate equation[7] is

$$\frac{D_{NCH}}{D_{HCH}} = \frac{\gamma_N}{\gamma_H}\left(\frac{r_{HCH}}{r_{NCH}}\right)^3\left[\left(\frac{r_{NCH}}{r_{HCH}}\right)^2 - 2\right] \qquad (7)$$

Utilizing the dipole couplings listed in Table II

$$r_{HCH}/r_{NCH} = 0.8471 \pm 0.0027 \qquad (8)$$

The angle γ of Figure 2B is now determined as 20.28 ± 0.1°. The ratio given in (8) compares with the value 0.8494 for the corresponding situation in the methylammonium ion.[13] The assumption that $r_{CH} = 1.096$ Å may now be introduced to compute the carbon position and various other angles and distances as before.[13] The diagram 2B can be used to verify the following relation

$$C = a\cos\gamma \pm [a^2\cos^2\gamma - a^2 + b^2]^{1/2} \qquad (9)$$

Three possible distances for $a = r_{CN}$ may be reasonably taken. The X-ray diffraction study[17] suggests two possible bond lengths 1.455 and 1.476 Å[17] while the NC bond length determined by us for the methylammonium ion is 1.488 Å.[13] Using (9) to compute "c" from Figure 2B gives three corresponding distances 2.1027, 2.1121, and 2.1174, respectively. "r_{HCH}" can now be computed as the three values 1.7812, 1.7891, and 1.7936 Å, respectively. The angle α again with corresponding values in order is 108.70, 109.41, or 109.82°. The angle HCH = α is likely to be somewhat greater than the tetrahedral angle as found for the methylammonium ion.[13] The values $r_{CH} = 1.096$ Å (assumed), $\gamma = 29.28°$, $r_{CN} = 1.488$ Å (assumed), $c = 2.1174$ Å, $r_{HCH} = 1.7936$ Å, $\alpha = 109.82°$, and $r_{NCH} = 2.1173$ Å ·for the CH_3N moiety give a somewhat better consistency with the nmr studies of the methylammonium ion than do the values from the X-ray structure determination. The NC bond length 1.455 Å obtained in the X-ray diffraction study appears to be somewhat short. Some recalculation of the angle ϕ_{xx} is possible from the values $r_{HCH} = 1.7936$ Å and $r_{NC} = 1.488$ Å. Using the following expression for S_{C_3}[7]

$$S_{C_3} = +D_{HCH}r_{HCH}^3/120,067 \text{ Hz Å}^3 \qquad (10)$$

with $D_{HCH} = -112.75$ Hz (Table II), $S_{C_3} = -5.4184 \pm 0.0025 \times 10^{-3}$. Then with $S_{yy} = 0$ and value $S_{xx} = -7.6732 \times 10^{-3}$, an equation similar to (1) gives $\phi_{xx} =$
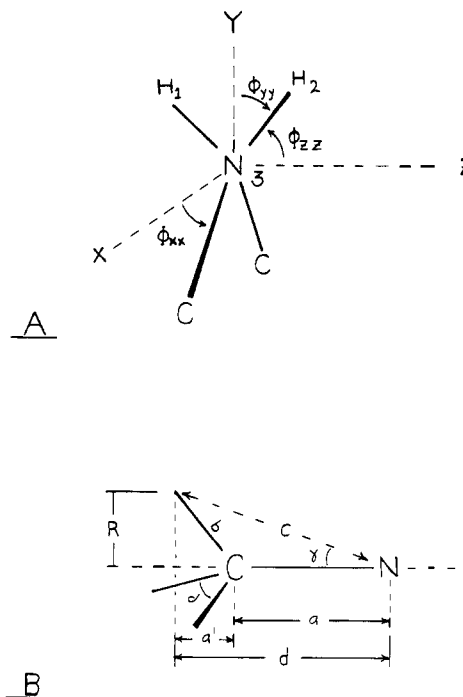
_A_

_B_

Figure 2. (A) Molecule based Cartesian coordinate system for description of the degree of orientation of the dimethylammonium ion. The y axis bisects HNH, the x axis is perpendicular to the HNH plane, and the z axis is perpendicular to the CNC plane and in the HNH plane. The angles ϕ_{yy} and ϕ_{zz} are those between the NH bond direction and the y and z directions, respectively. ϕ_{xx} is the angle betweeen the NC bond and the x axis. (B) A diagram of the local C_{3v} symmetry at each CH_3-N moiety: b = length of CH bond, c = distance from carbon proton to nitrogen, a = CN bond length, a' = projection of the CH bond on the CN axis, $d = (a + a')$, α = angle HCH, γ = angle HNC. Atoms are numbered for reference purposes in text and tables, e.g., $r_{12} = r_{HNH}$ the distance between NH_2^+ protons.

32.83°. Thus the angle CNC is adjusted to 114.3°. This appears a much more reasonable value.

The other dipole-dipole couplings derived from the nmr spectrum of the oriented ion $D_{HNCH} = 39.17$ Hz and $D_{H_3CNCH_3} = 49.31$ Hz are dependent on the hindered internal rotation of the two methyl groups. This problem will not be attempted at this stage, except to point out that the distance of closest approach of the two circles on which the methyl protons rotate can be computed as 1.9796 Å from the most reasonable parameters of other angles and distances in the ion. This distance is somewhat less than the sum of van der Waals radii of two bonded hydrogen atoms. Some hindered rotation may be expected from this purely steric source, but it is still an open question as to whether rotation of the two methyl groups is geared, partially geared, independent and hindered, or independent and free.[7] The closest approach of methyl and NH_2^+ protons may be computed from these geometric parameters·and it is 2.180 Å.

The dipole-dipole coupling constants obtained from the trimethylammonium ion in Table II do not give sufficient information to discuss the structure of the ion. The spectrum $A_3A_3'A_3''$ is already quite complex while on the other hand we were unable to obtain a good analysis of the $A_3A_3'A_3''B$ spectrum because of the number of overlapping transitions. It is possible that a higher ordering middle phase could be found and that then N-15 and C-13 isotopic enrichment would become worthwhile. The determination of all internuclear distance ratios in the trimethylammonium ion is about the maximum complexity acceptable in ion structures at the present time.

The failure to observe any dipole–dipole coupling in the $N(CH_3)_4^+$ ion is not proof that the ion is not ordered. The increase in line width over the spectrum recorded for isotropic solutions leads us to expect nuclear quadrupole splitting for the deuterated ion in middle nematic phases. The N-14 spectrum is an even more sensitive test of small degrees of orientation.[10-12] Increasing the number of methyl groups in methylammonium ions must increase the ability of the ion to penetrate the electrical double layer of the phase and thus to reside partly in the lipophilic region. We are unable, without further study, to obtain evidence on this important question.

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Reactions Involving Hydrogen Peroxide, Iodine, and Iodate Ion. V. Introduction to the Oscillatory Decomposition of Hydrogen Peroxide[1]

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Abstract: Apparatus is described that permits the simultaneous recording of three (oxygen, iodine, iodide) among the kinds of pulses that characterize the oscillatory decomposition of hydrogen peroxide in this reaction system. For two significant experiments of identical composition, such recordings joined to gas-buret readings give a body of evidence unusual in precision and extent for oscillatory reactions. This evidence makes possible a thorough test of an updated skeleton mechanism based upon extensive earlier work. The results of the test are encouraging but not conclusive.

The investigations to which this series belongs are separated chronologically as follows: 1916–1917, when the oscillatory decomposition was discovered;[2] 1927–1933, when the whole reaction system was surveyed and the isolation of individual reactions was begun;[3-5] 1967 to the present,[6-14] when modern experimental methods were introduced and necessary ancillary work was done.

Extensive experiments, many of which, though useful, will not be published because they were exploratory in nature, have led to an updated skeleton mechanism to be tested here against the results of two of the most significant experiments among the multitude.
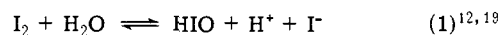
Updated Skeleton Mechanism

The complex chemistry of this reaction system (ref 2, Table I) implies a complicated mechanism in which the same set of reactions must vary widely enough in rate at different concentrations of hydrogen peroxide, acid, iodate, iodine, and iodide to explain the results observed. By "skeleton" is meant that species such as HIO_3, $H_2I_2O_6$, and congeners,[15] $H_2I_2O_3$ and congeners,[5,10,16,17] and free radicals; all these will be reserved for future introduction if needed.

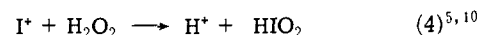The original point of departure[2] for the present mechanism was the "simplest direct line between iodide and periodate in acid solution," which is I^-, HIO, HIO_2, IO_3^-, IO_4^-.

Thermodynamics establishes the likelihood that H_2O_2 can oxidize each substance in this line except the last and reduce each except the first. Periodate species are safely dismissed from further consideration.[3] Thermodynamics thus predicts the possibility that H_2O_2 will be catalytically decomposed in reaction systems containing the first four iodine species in the line, but only kinetic experiments can establish whether such catalysis actually occurs, by what mechanism, and of what nature (smooth, oscillatory, or both). The H_2O_2-Br_2-Br^- reaction system,[18] in which only smooth decomposition occurs, is valuable as a simple standard of comparison for the present system, which is now presumed to have the following mechanism.

Reversible reactions

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (1)^{[12,19]}$$

$$I_2 \rightleftharpoons I^+ + I^- \qquad (2)^{[10,20]}$$

$$2H^+ + IO_3^- + I^- \rightleftharpoons HIO + HIO_2 \qquad (3)^{[5,11,16]}$$

Oxidation of I^+

$$I^+ + H_2O_2 \longrightarrow H^+ + HIO_2 \qquad (4)^{[5,10]}$$

Reduction of HIO

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2 \qquad (5)^{[10,21]}$$