

Table IV. Zero Field Splittings of Biradical Ion Clusters of Radical Ions Containing Heteroatoms

Anion	Cation	Solvent	Fine structure splitting, G
Quinoxaline	Li	MTHF	79.3
Terephthalonitrile	Li	MTHF	47.8
4-Chloronitrobenzene	Li	MTHF	111.9
Anthraquinone	Li	THF	20

the solution epr spectra of these species are due to higher ion clusters rather than solvent-separated triple ion biradicals.

(VI) **Paramagnetic Ion Quadruplets in Other Systems.** The various forms of paramagnetic and diamagnetic ion clusters such as discussed here are likely to exist commonly in the solutions of other radical ions containing heteroatoms. In order to establish the general existence of paramagnetic ion clusters in other types of systems, we have investigated the rigid media epr spectra of MTHF solutions of the radical anions of quinoxaline, terephthalonitrile, 4-chloronitrobenzene,³³ and anthraquinone. These systems gave relatively strong rigid media epr spectra at 10^{-3} in MTHF. Fine structure splittings of these systems are given in

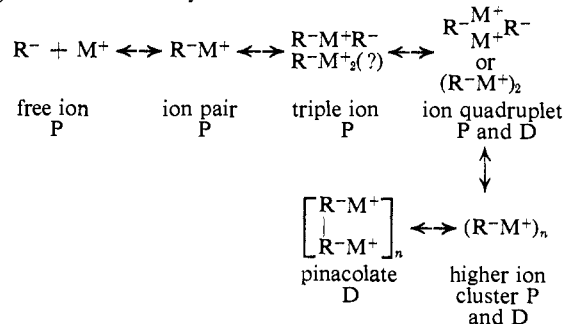
(33) A paramagnetic ion cluster of the nitrobenzene anion was reported by C. A. McDowell and F. Nakano, *J. Phys. Chem.*, **75**, 1205 (1971).

Table IV. Various forms of ionic species such as discussed in this paper may exist in these solutions.

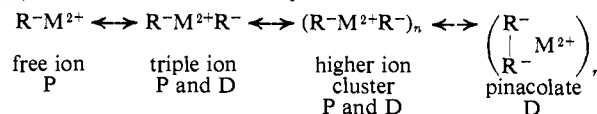
Conclusions and Summary

The equilibrium scheme for ketyls is summarized as follows.

(a) Alkali metal ketyls



(b) Alkaline earth metal ketyls



P and D stand for paramagnetic and diamagnetic species.

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Studies of Membrane Processes. IV. Structure of the Acetate Ion and Degree of Orientation of the Ionic Head Groups in the Electrical Double Layer¹

D. M. Chen,^{2a} L. W. Reeves,^{*2a,b} A. S. Tracey,^{2c} and M. M. Tracey^{2c}

Contribution from the Instituto de Química, Universidade de São Paulo, São Paulo, Brazil, and the Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada. Received November 15, 1973

Abstract: A model membrane based on the cationic detergent decylammonium chloride has been prepared and studied. Nematic middle soap phases of this detergent have been used to homogeneously orient the acetate ion and simultaneously the lipophilic region of the model system. The structure of the acetate ion has been determined, apart from the oxygen positions, by studying nuclear magnetic resonance spectra of oriented $1\text{-}^{13}\text{C}$ and $2\text{-}^{13}\text{C}$ acetate. In other experiments the acetate and perdeuterioacetate ions have been oriented in the same phase, and by studying both the proton and deuterium magnetic resonance spectra the deuterium nuclear quadrupole coupling constant in the acetate ion has been determined. Similar nematic middle soap phases have been prepared from the 1,1,1,1,2,2-pentadeuterated decylammonium detergent. The deuterium magnetic resonance spectra are composed of three doublets arising from first-order quadrupolar interactions at the terminal -ND_3^+ , adjacent $\text{-CD}_2\text{-}$, and D_2O nuclei. The variation of the partially averaged quadrupole splitting in these ionic and methylene head groups of the membrane electrical double layer have been measured as a function of temperature. Very large temperature dependence of the local microdegree of orientation is indicated over small temperature ranges between 24.5 and 33.5° . A consideration of degrees of order of small ionic and molecular species, which reside mostly in the aqueous region of the phase, and those of the head groups in the electrical double layer has shown that movement of the head groups is considerably restricted. A clearer picture of this membrane model has emerged from studies of deuterium magnetic resonance spectra and these in turn have indicated that further studies of specifically deuterated lipophilic components in these phases are required.

The oriented superstructures of the middle soap nematic phases consist of cylindrical arrangements

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of the ionic head groups of detergent ions. The in-

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(2) (a) University of Waterloo; (b) visiting professor since 1967 at the Universidade de São Paulo; (c) Universidade de São Paulo.

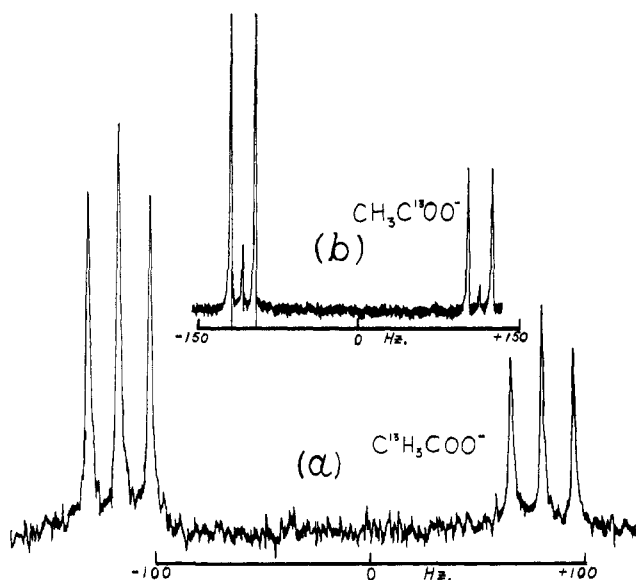


Figure 1. (a) The proton magnetic resonance spectrum of the $1\text{-}^{13}\text{C}$ (60% enriched) acetate ion oriented in nematic phase a at 60 MHz. Low-field components of the overall triplet structure are omitted. (b) The proton magnetic resonance spectrum of the $2\text{-}^{13}\text{C}$ (90% enriched) acetate ion oriented in nematic phase b at 100 MHz. Low-field components are omitted.

terior of the cylinders consists of the hydrophobic hydrocarbon chains while the aqueous interstitial region contains the counterions to the ionic head groups.³ The essential constituents of a membrane are present and it is possible to distinguish three regions: (a) the hydrocarbon chains, (b) the electrical double layer interface which contains the ionic head groups with some attached counterions, and (c) the aqueous region which contains some free counterions.

The power of the nuclear magnetic resonance (nmr) technique in studying model membrane processes depends upon the ability of the magnetic field to induce homogeneous orientation of the cylindrical superstructure by producing a torque *via* the large diamagnetic anisotropy of the macroscopic order.⁴⁻⁸ The nmr experiments are performed therefore on a highly ordered sample.

This series of papers is concerned with membrane processes in all three essential regions of the model system. In this particular study we discuss the structure of the acetate ion in a cationic detergent model system, the deuterium quadrupole coupling constant in the CD_2COO^- , and the degree of orientation of the $-\text{ND}_3^+$ and $-\text{CD}_2-$ groups in the electrical double layer.

(3) G. H. Brown, J. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.

(4) (a) V. Luzzatti and F. Reiss-Husson, *Nature (London)*, **210**, 1351 (1966); (b) V. Luzzatti, H. Mustacchi, A. Skoulis, and F. Reiss-Husson, *Acta Crystallogr.*, **13**, 660 (1960); (c) V. Luzzatti and F. Reiss-Husson, *Advan. Biol. Med. Phys.*, **11**, 87 (1967).

(5) L. Mandell, K. Fontell, and P. Ekwall, *Advan. Chem. Ser.*, No. **63**, 89 (1967).

(6) (a) L. W. Reeves, J. M. Riveros, R. A. Spragg, and J. A. Vanin, *Mol. Phys.*, **20**, 9 (1973); (b) S. A. Barton, M. A. Raza, and L. W. Reeves, *J. Magn. Resonance*, **9**, 45 (1973); (c) L. W. Reeves, V. R. Vanin, and J. A. Vanin, *An. Acad. Brasil. Cienc.*, **44**, 314, 431 (1972).

(7) (a) L. W. Reeves, A. S. Tracey, and M. M. Tracey, *J. Amer. Chem. Soc.*, **95**, 3799 (1973); (b) L. W. Reeves, J. Sanches de Cara, M. Suzuki, and A. S. Tracey, *Mol. Phys.*, **25**, 1481 (1973); (c) D. M. Chen and L. W. Reeves, *J. Amer. Chem. Soc.*, **94**, 4384 (1972).

(8) (a) L. W. Reeves and A. S. Tracey, *J. Amer. Chem. Soc.*, **96**, 365 (1974); (b) *ibid.*, **96**, 1198 (1974); (c) L. W. Reeves, M. Suzuki, A. S. Tracey, and J. A. Vanin, *Inorg. Chem.*, **13**, 999 (1974).

The cylindrical superstructure⁴ has a high degree of orientation approaching the value $-\frac{1}{2}$ ³ as measured by various techniques and it becomes an interesting question to investigate by nmr the microdegree of orientation of ionic head groups of individual detergent ions which form the immobilized half of the electrical double layer. The acetate ion is the mobile component of the electrical double layer region and is involved in an equilibrium exchange process between interstitial water and the surfaces of the charged cylinders.

Experimental Section

(1) **Cationic Middle Phases.** The model membrane systems used here are based on the cationic detergent phase^{7a} made from decylammonium salts. Several phases were prepared from decylammonium acetate, which was synthesized by neutralization of decylamine with acetic acid. The aqueous solution was evaporated and the detergent salt recrystallized from ethyl acetate. For deuterium-labeled counterions, deuterioacetic acid was used as the starting material (99.8% D substituted in the methyl group). Sodium $1\text{-}^{13}\text{C}$ -acetate (60% enrichment) and sodium $2\text{-}^{13}\text{C}$ -acetate (90% enrichment) supplied by Merck Sharp and Dohme were used for the ^{13}C enriched compounds. In some experiments the 1,1,1,2,2-pentadeuterated decylammonium ion was used.

(2) **Preparation of 1,1,1,2,2-Pentadeuteriododecylamine.** During a time of 45 min, 46 ml of redistilled thionyl chloride was added to 86 g of decanoic acid in a three-necked flask, equipped with a condenser and a dropping funnel. To complete the reaction the solution was refluxed for 30 min. Excess thionyl chloride was removed by distillation and the acid chloride was then distilled under reduced pressure (1 cm). Ammonia solution (125 ml of 0.88 M) was chilled to ice temperature in an ice bath. The acid chloride of decanoic acid was added slowly with constant stirring. The decylamide separated and was removed by filtration and then air dried. The decylamide was then reduced to decylamine in the following manner. Lithium aluminum deuteride (5 g) (Merck Sharp and Dohme) dissolved in 50 ml of diethyl ether was added to 10 g of decylamide in 150 ml of diethyl ether. The mixture was refluxed for 16 hr. Water was then added to decompose the remaining lithium aluminum deuteride and the solution filtered. Removal of the ether layer and evaporation gave the crude product. The deuterated decylamine was purified by distillation under reduced pressure to yield 2.5 g of pure material.

(3) **Compositions of Middle Phases.** The phases used in this study had the following compositions: (a) 33.1 wt % decylammonium chloride (DACl), 5.0% sodium $1\text{-}^{13}\text{C}$ -acetate, 2.4% decanol, and 59.5% by weight D_2O ; (b) 33.2% DACl, 4.9% sodium $2\text{-}^{13}\text{C}$ -acetate, 2.4% decanol, and 59.5% D_2O ; (c) 17% DACl, 2.8% ammonium chloride, 4.2% decylammonium acetate, 24.8% 2,2-dideuteriododecylammonium acetate- d_3 , 3.4% decanol, and 47.8% H_2O ; (d) 26.2% 1,1,1,2,2-pentadeuteriododecylammonium acetate- d_5 , 2.8% ammonium chloride, 16.2% DACl, 3.0% decanol, and 51.8% D_2O . Several other similar phases were prepared but all fell into the above categories of compositions type a, b, c, or d. The results section will proceed under the headings of these different phase types.

(4) **Nmr Measurements.** The scalar couplings between carbon-13 and hydrogen were determined from isotopic aqueous solutions of the following composition: 16.6 wt % sodium $1\text{-}^{13}\text{C}$ -acetate and 17.0 wt % sodium $2\text{-}^{13}\text{C}$ -acetate.

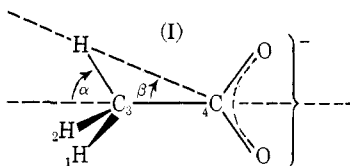
Proton magnetic resonance spectra were recorded on a Varian T60 spectrometer with a probe temperature of $34.0 \pm 0.1^\circ$. Deuterium magnetic resonance spectra were recorded in several ways. For broader resonances a Varian VF16 spectrometer was used with audio modulation of 40 Hz and a lock-in detector. Radiofrequencies used for the observation were either 4.1 or 7.1 MHz and the probe temperature was 29.6 ± 0.1 and $31.7 \pm 0.2^\circ$, respectively. Spectra were calibrated by resetting the frequency of a Schomandl frequency synthesizer, used to drive the radiofrequency unit of the VF16. The frequency setting of the synthesizer could be changed at the termination of a spectrum and while still sweeping; the spectrum was then repeated at a second or third calibrated frequency. The modulation frequency of 40 Hz causes some broadening of the D_2O signals in the phase.

Deuterium nuclear magnetic resonance was also performed using a 7.95-MHz V4311 radiofrequency source from Varian with an HR60 spectrometer. Samples could be 10- or 5-mm external diam-

eter. In cases of poor signal strengths such as the spectrum from oriented CD_3COO^- the free induction decay from a home built Fourier transform spectrometer was accumulated onto a 4K Fabritek 1074 signal averager. The averaged signal was transferred to a PDP-11 and processed to the frequency mode by an IBM 360/75. The resultant spectra were then presented by a Calcomp plotter display. The basic details of this spectrometer have been previously submitted to the literature in a study of ^{205}Tl magnetic resonance.⁹

Results

(1) Nematic Phases Type a. The purpose of this lyotropic nematic phase was to partially orient the $1\text{-}^{13}\text{C}$ acetate ion and to measure the values $|^1D_{\text{CH}} + ^1J_{\text{CH}}|$ from the spectrum. As shown in Figure 1a the spectrum of the isotropically substituted acetate ion is a triplet derived from the $\sim 40\%$ abundant ^{12}C species and each feature of this is doubled for the 60% ^{13}C substituted methyl group. The triplet derives from dipole-dipole coupling between equivalent protons in the methyl group and the separations of 194.0 Hz are equal to $^3/2D_{\text{HH}}$.¹⁰ The acetate ion is labeled according to the numbered positions below.



The value of $J_{13} = J_{23}$ derived from spectra in isotropic aqueous solutions was $+126.6 \pm 0.1$ Hz. In company with all other couplings between directly bonded C-H's the absolute positive sign is assumed. From spectra such as that shown in Figure 1a the value $D_{12} = D_{\text{HH}} = \pm 129.35 \pm 0.1$ Hz was derived from the triplet while the value $D_{\text{CH}} = D_{13} = D_{23} = -156.68$ or -96.52 was obtained from the doublet structure. The sign and value ambiguities derive from the lack of knowledge of the signs of the dipolar couplings only. The magnitude of these dipolar couplings, of course, reflects the degree of orientation.

(2) Nematic Phase Type b. This phase yields the dipolar couplings between methyl protons $D_{\text{HH}} = D_{12}$ and the magnitude $|D_{14} + J_{14}|$. The spectrum of the oriented ion is presented as Figure 1b. The value of J_{14} obtained from isotropic aqueous solutions of the ion is ± 5.74 Hz. This coupling is known to have a negative absolute sign but both signs can be accepted for the time being, since further analysis distinguishes the correct direction of the magnitude. The measured magnitude of D_{12} in this phase is ± 147.74 Hz while $D_{14} = D_{24}$ is either ± 16.55 or ± 28.03 Hz. Error limits are on the order ± 0.1 Hz.

(3) The Ratios of Dipole-Dipole Coupling Constants. The ratio of dipole-dipole coupling constants for an AX_3 spectrum can be given in simple terms¹⁰ if there is a C_3 symmetry axis.

$$\left(\frac{D_{\text{AX}}}{D_{\text{XX}}}\right) = \left(\frac{\gamma_{\text{A}}}{\gamma_{\text{X}}}\right) \left(\frac{r_{\text{XX}}}{r_{\text{AX}}}\right)^3 \left[\left(\frac{r_{\text{XX}}}{r_{\text{AX}}}\right)^2 - 2 \right] \quad (1)$$

r_{XX} and r_{AX} are internuclear distances while γ_{A} and γ_{X} are magnetogyric ratios of the A and X nuclei. The ratio D_{13}/D_{12} can have values ± 1.21131 or ± 0.74621

while the ratio D_{14}/D_{12} can have values ± 0.18975 or ± 0.11204 . The elimination of the incorrect signs and magnitudes can be made on the basis of a reasonable structure. The only internuclear distance ratios which are acceptable from eq 1 are $r_{12}/r_{13} = 1.6363$ and $r_{12}/r_{14} = 0.8329$. These ratios correspond to the dipole coupling ratios $D_{13}/D_{12} = +0.7462$ and $D_{14}/D_{12} = -0.1898$. This corresponds to the correct choice of $J_{14} = -5.74$ Hz which agrees with earlier relative sign determinations for $^2J_{\text{CCH}}$.¹¹ The angles in the CH_3C moiety are now determined as $\angle \text{H}_1\text{C}_3\text{C}_4 = 109.14^\circ$, $\angle \text{H}_1\text{C}_3\text{H}_2 = 109.80^\circ$, $\angle \text{C}_3\text{C}_4\text{H} = \beta = 28.74^\circ$, and $\angle \alpha = 70.86^\circ$. The error bounds, which derive from random sources only, are ± 0.0002 for the distance ratios and $\sim \pm 0.05\%$ in the angles.

The distance r_{12} between methyl protons can be used as a reference distance of 1.793 Å to give a refined structure presented as Table I.

Table I. Refined Parameters for the Carbon and Hydrogen Positions in the Acetate Ion Determined from Nuclear Magnetic Resonance Spectra of Oriented $1\text{-}^{13}\text{C}$ Acetate and $2\text{-}^{13}\text{C}$ Acetate Ions in Phases a and b Described in the Text

$r_{\text{H}_1\text{H}_2} = 1.793 \text{ \AA}$ (assumed)	$\angle \alpha = 70.86 \pm 0.05^\circ$
$r_{\text{H}_1\text{C}_3} = 1.096 \pm 0.001 \text{ \AA}$	$\angle \beta = 28.74 \pm 0.07^\circ$
$r_{\text{H}_1\text{C}_4} = 2.154 \pm 0.001 \text{ \AA}$	$\angle \text{H}_1\text{C}_3\text{H}_2 = 109.80 \pm 0.05^\circ$
$r_{\text{C}_3\text{C}_4} = 1.529 \pm 0.001 \text{ \AA}$	$\angle \text{H}_1\text{C}_3\text{C}_4 = 109.14 \pm 0.05^\circ$

(4) Nematic Phase Type c. One of the purposes of studying the nuclear magnetic spectra of this phase was to simultaneously orient the ions CH_3COO^- and CD_3COO^- in relative abundance 10:90 in the same medium. A study of the proton magnetic resonance of the oriented 10% CH_3COO^- leads to a determination of dipole-dipole coupling $D_{12} = D_{\text{HH}}$. By use of the simple relationship below for the degree of orientation with the now known structure of the ion, *i.e.*, $r_{\text{HH}} = r_{12}$, the former can be determined.

$$D_{\text{HH}} = -\frac{1}{2} \frac{h\gamma_{\text{H}}^2}{\pi^2 r_{\text{HH}}^3} S_{\text{HH}} \quad (2)$$

S_{HH} is the degree of orientation of the H-H axis and γ_{H} is the magnetogyric ratio of the proton. The factor $h\gamma_{\text{H}}^2/\pi^2 = 240,134 \text{ Hz \AA}^3$. The degree of orientation of the deuterated acetate ion is assumed to be the same as that of the proton containing ion and this has been justified by some recent work from this laboratory on the orientation of ND_4^+ and ND_3H^+ .^{8a} Even with the symmetry change T_d to C_{3v} between ND_4^+ and ND_3H^+ , there is no significant change in degree of orientation.

The structure determined for the acetate ion using phases a and b will now be used to determine the nuclear quadrupole coupling constant for the deuterium in CD_3COO^- . The proton magnetic resonance spectra of phase c gave $D_{\text{HH}} = D_{12} = -161.67 \pm 0.1$ Hz, and with an assumed value $r_{12} = r_{\text{HH}} = 1.793 \text{ \AA}$ the degree of orientation of the threefold axis of the CH_3C moiety was obtained as $S_{\text{C}_3} = -7.76 \times 10^{-3}$ from the relation $-1/2 S_{\text{C}_3} = S_{\text{HH}}$. The two axes are always perpendicular. The deuterium nmr spectrum of the CD_3COO^- required some enhancement by Fourier trans-

(9) S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **96**, 404 (1974).

(10) P. Deihl and C. L. Khetrapal, "NMR—Basic Principles and Progress," Vol. 1, P. Deihl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N. Y., 1969, Chapter 1, p 1.

(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1966.



Figure 2. The deuterium magnetic resonance spectrum of lyotropic nematic phase d after separation of the bottom isotropic phase. The upper phase, which was studied, was a typical mobile nematic phase. The outer doublet is assigned to partially averaged nuclear quadrupole coupling in the deuterium atoms of the $-\text{CD}_2-$ group and the inner doublet arises from the adjacent $-\text{ND}_3^+$ group. The deuterium signal of the D_2O was overmodulated at the center of the spectrum and has been omitted. The detection frequency was 4.1 MHz and the temperature 28° .

form methods. Five spectra were recorded with between 512 and 1024 scans at a pulse interval of 0.63 sec and at different frequency offsets. The spectrum appeared as a doublet of average separation $\Delta\nu_Q = |672 \pm 3 \text{ Hz}|$. The maximum error rather than the mean square deviation of values is cited for the five spectra. The doublet separation $\Delta\nu_Q$ can be given in terms of the quadrupolar coupling constant and the degree of orientation of the C_3 axis S_{C_3} ,^{8a}

$$\Delta\nu_Q = \frac{3}{2}Q_D \frac{1}{2}(3 \cos^2 \alpha - 1)S_{C_3} \quad (3)$$

α is the angle between the C_3 axis and the C-H bond designated in structure I earlier. Q_D is the nuclear quadrupole coupling constant of the deuterium assuming a negligibly small asymmetry parameter η and a principal axis along the C-D bond. The value of Q_D obtained is $170.4 \pm 0.8 \text{ KHz}$ using $\alpha = 70.86^\circ$ derived earlier. This value is to be compared with other known deuterium quadrupole coupling constants in C-D bonds.¹² The compilation of Millett and Dailey¹² cites some 30 known value of Q_D from the literature and the presently determined value is a very reasonable one considering similar compounds; it also has a small probable error compared to previous measurements since it is determined from the known geometry obtained here.

Nematic phase c was made up with H_2O but with 2,2-dideuteriododecylammonium acetate so that using the broad line spectrometer the deuterium resonance in the first methylene group attached to the $-\text{NH}_3^+$ head group could be detected. This enables us to use the quadrupole coupling constant to investigate the degree of order in the hydrocarbon chain region of the lyotropic nematic phase. The signal of the $-\text{CD}_2-$ group was a broadened doublet of separation 9.57 kHz. If we assume the quadrupole coupling constant in this $-\text{CD}_2-$ group as 170 kHz interpolating from the data presented by Millett and Dailey, the degree of orientation along the C-D bond (S_{C-D}) from the expression

$$\Delta\nu_{CD} = \frac{3}{2}Q_{CD}S_{CD} \quad (4)$$

becomes 0.038 with the sign uncertain.

(5) Nematic Phase Type d. The deuterium oxide used to make this phase was acidified with a few drops of sulfuric acid so to sufficiently slow down the deuterium exchange between the water and the $-\text{ND}_3^+$ groups of the decylammonium ion in the phase. The quad-

rupole splitting of the D_2O and $-\text{ND}_3^+$ groups could be observed separately in the deuterium nmr spectrum. The water (D_2O) content of this phase exceeded the limit of stability of the nematic region and a lower phase of equal volume which was not birefringent separated. The less dense upper nematic phase was separated for study. The birefringent upper phase was identified with the single phases a, b, and c described here by mixing to form single nematic phases.

In Figure 2 the deuterium spectrum of the nematic phase is presented for a detection frequency of 4.1 MHz and a temperature 28° . The audio lock-in detector of the VF16 spectrometer was most satisfactory in displaying the rather broad peaks. The overmodulated D_2O doublet has been omitted from the center of the spectrum. The outer doublet from the $-\text{CD}_2-$ group has a separation $|\Delta\nu_Q| = 14.5 \text{ kHz}$ while the inner doublet from the $-\text{ND}_3^+$ group has a splitting $\Delta\nu_Q = 6.1 \text{ kHz}$.¹³ At this temperature the separation of the doublet is consistent with the corresponding $\Delta\nu_Q = 9.57 \text{ kHz}$ in nematic phase c for the $-\text{CD}_2-$ group. The splitting of 6.1 kHz for the inner doublet is consistent with work¹³ for which no $-\text{CD}_2-$ group is present.

A variable temperature deuterium magnetic resonance study of the two doublets was made at 7.1 MHz between 24.5 and 37.2° . There was a separation of a small amount of the isotropic phase in a lower layer as the temperature was raised in the range above 34° . At the higher temperatures a signal at the center of the D_2O doublet appeared, which was assigned to a signal from the second isotropic phase. On separation of the second phase at 33.5° the doublet separation remained the same up to 37.2° which was the limit of practical study for the system. Between 24.5 and 33.5° the change in partially averaged quadrupole coupling for the $-\text{ND}_3^+$ group was very large as can be seen displayed in Table II.

Table II. Partially Averaged Quadrupole Coupling Constants in the Head Ionic Group $\Delta\nu_Q(-\text{ND}_3^+)$ and the Adjacent Methylene Group $\Delta\nu_Q(-\text{CD}_2-)^a$

Temp, ^b °C	$\Delta\nu_Q(\text{ND}_3^+)$, kHz	$\Delta\nu_Q(-\text{CD}_2-)$, kHz	$\Delta\nu_Q(\text{CD}_2)/\Delta\nu_Q(\text{ND}_3^+)$
24.5	7.3	17.4	2.38
26.0	6.6	15.6	2.37
26.8 ^c	6.4	15.7	2.45
28.0	6.1	14.5	2.40
30.0	5.6	13.5	2.41
31.5	4.9	11.7	2.39
33.5 ^d	4.7	11.2	2.38
34.5 ^d	4.7	11.2	2.38
35.0 ^d	4.8	11.5	2.34
37.2 ^d	4.7	11.2	2.38

^a These values are proportional to the microdegree of order along the N-D and C-D bond directions, respectively. The standard errors in measurement up to the two-phase region 33.5 to 37.2° is $\pm 0.1 \text{ kHz}$. The large temperature dependence of the microdegree of order in the electrical double layer of the model membrane is illustrative of the large variation in local motion as the temperature is varied and thus the rather small range over which such electrical double layers are macroscopically stable. The ratio of the partially averaged quadrupole couplings is always 2.39 ± 0.03 for the ND_3^+ and the $-\text{CD}_2-$ groups because their motions are directly connected by the common N-C bond. ^b Temperature controlled to $\pm 0.3^\circ$. ^c 4.1 MHz. ^d A two-phase region, the lower one isotropic.

(12) F. S. Millett and B. P. Dailey, *J. Chem. Phys.*, **56**, 3249 (1972).

(13) F. Fujiwara and L. W. Reeves, unpublished results.

Discussion

(1) **Structure of the Acetate Ion.** To compare with the structure derived here for the acetate ion, there are some studies of the parent acid where the positions of all atoms except hydrogen have been investigated.^{14,15} In the vapor phase¹⁴ the structures of the monomer and dimer have been derived while the X-ray diffraction study¹⁵ of Jones and Templeton shows that the acid crystallizes with polymeric hydrogen bonded chains. In this study we have been unable to determine oxygen positions in the ion. In the parent acid the C-C bond length of $1.54 \pm 0.02 \text{ \AA}$ compares with our value here of $1.529 \pm 0.001 \text{ \AA}$. The extensive study of Dunell, Reeves, and Strømme¹⁶ of proton magnetic resonance signals in polycrystalline CH_3COOD , CD_3COOH , and CH_3COOH departs from the structure of Jones and Templeton in the solid state but with the additional and important assumptions of tetrahedral bond angles in the CH_3^- groups and a C-H bond length of 1.094 \AA . These assumptions are justified by the present study of the ion, where we find angles at the CH_3^- group very close to tetrahedral (Table I) and a CH bond length of $1.096 \pm 0.001 \text{ \AA}$. It is not expected that changes from the acid to the ion will significantly affect the distance and angle in the CH_3C moiety. The crystal structure of the hydrates of metal acetates determined by X-ray diffraction methods have been concentrated on the positions of oxygen in hydrate water and acetate ions with respect to the metal ion.^{17a-c} The C-C bond length in nickel acetate tetrahydrate was determined as 1.56 \AA .

(2) **Degree of Orientation of Ions and Molecules.** The three regions of a middle soap phase, mentioned in the introductory section of this article, are (a) hydrocarbon chains, (b) electrical double layer, and (c) aqueous region.¹⁸ As Winsor¹⁸ has pointed out, there is considerable evidence for penetration of water into the lipophilic region in micellar and middle phase systems.^{4a-c, 19a-c} The chemical shift changes of terminal $-\text{CF}_3$ groups in micelles of sodium 12,12,12-trifluorododecyl sulfate measured by Muller and Birkhahn²⁰ indicate an environment between that of an aqueous and hydrocarbon solution. In an earlier study from these laboratories the environment of the dimethyltin ion in the middle phase has been shown to be quite different from that in isotropic aqueous solution.^{8c} The degree of orientation on the microscopic scale of single molecules and ions as opposed to the degree of orientation of the macroscopic optic axis of the phase is indicative of the motional freedom of individual constituents of the phase. The overall long range order in cylindrical superstructures can be preserved while at the same time allowing considerable motional averaging of molecular

and ion orientation. On a microscopic scale, diffusion of water and ions into the rather disordered electrical double layer¹⁸ and even into the interior region of the cylinders leads to small degrees of orientation. Table III is presented to illustrate typical degrees of ori-

Table III. Microscopic Degrees of Orientation of Species in Anionic and Cationic Middle Nematic Phases Measured in These Laboratories

Phase	Species	Degree of orientation S_{C_3} or other specified axis	Temp, deg	Ref
DS ^a	(a) CH_3OH	$\pm 5.89 \times 10^{-3}$	31.1	8a
	(b) CH_3OH	$\pm 7.55 \times 10^{-3}$	31.1	8a
	(c) CH_3ND_3^+	-1.58×10^{-2}	31.1	8a
	(d) $\text{CH}_3\text{SnCH}_3^{2+}$	-1.37×10^{-2}	33.1	8c
DA ^b	(a) CH_3COO^-	-6.13×10^{-3}	31.1	This work
	(b) CH_3COO^-	-7.16×10^{-3}	31.1	This work
	(d) ^c $-\text{ND}_3^+$	± 0.164	29.5	This work
	$-\text{CD}_2^-$	± 0.136	29.5	This work

^a DS indicates an anionic detergent phase based on the dceyl sulfate ion. ^b DA indicates a cationic detergent nematic phase based on the decylammonium ion. The notations DA or DS (a), (b), (c), and (d) refer to four phases described in this work. For compositions of the anionic DA phases refer to previous work in ref 8a and 8c. In each case the S_{C_3} is referred to a C_3 axis perpendicular to the methyl groups. ^c The orientation of the $-\text{ND}_3^+$ and the $-\text{CD}_2^-$ moieties in the present cationic detergent phase is referred to an axis perpendicular to the superstructure walls. The angles used to resolve these degrees of orientation along the above axis are described in the text.

entation determined in this and earlier studies for ions and molecules in middle phases.⁸

From Table III some general indications can be seen. In the anionic detergent phases made up from sodium decyl sulfate the degrees of orientation of the methanol C-O bond are about the same as those of the C_3 axis of the ammonium ions in the same phase. The methylammonium ion which is more organic in nature has a degree of orientation higher than the ammonium ion and of the same order as the dimethyltin ion. The lower symmetry of these elongated ions is another factor which is expected to influence the higher degree of orientation. In cationic phases reported in this article the acetate ion in phases a, b, and c has remarkably similar degrees of orientation.

It is possible to suggest some aspects which merit further investigation. The phase itself is evidently a determining factor at a given temperature. It is clear also that the variation of the symmetry and the overall shape of the ion are important variables while the increasing ability to distribute into the hydrocarbon region should be further studied.

(3) **Degree of Orientation of the Head Groups of the Detergent.** The optic axes in the negative birefringent nematic middle soap phases¹⁸ are oriented perpendicular to the magnetic field and the indications are that the superstructure of the phase has a high degree of orientation which approaches -0.5 in a strong magnetic field. The small individual components such as small counterions, dissolved molecules, or water have a high degree of free movement in the phase of a diffusive type which leads to degrees of orientation which are not greater than 1.6×10^{-2} in the phases we have in-

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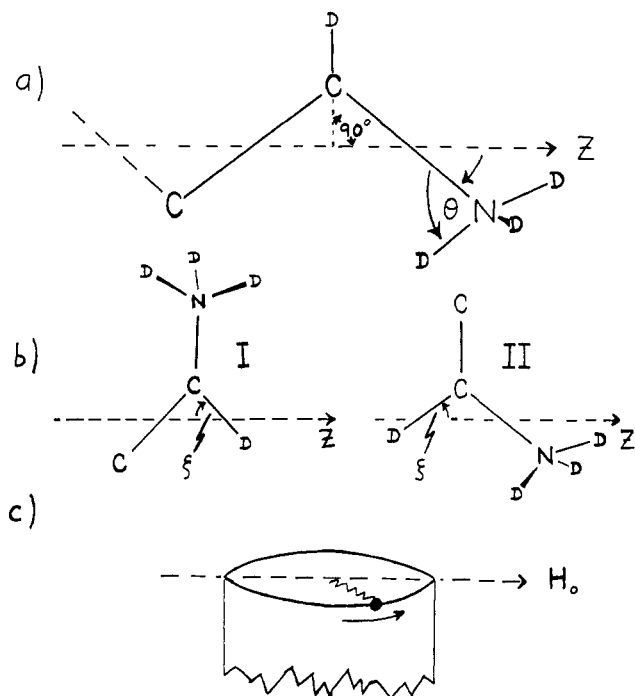


Figure 3. (a) Diagram showing the arrangement of the hydrocarbon chain in an extended conformation. The axis z is taken to be perpendicular to the surface of the superstructure. (b) I and II show other possible arrangements of the chain: (I) the terminal $-ND_3^+$ group no longer points at the surface, (II) the complete hydrocarbon chain is displaced but the $-ND_3^+$ group retains its orientation in the surface. (c) This motional averaging arises because the detergent ion may laterally diffuse around the superstructure or the cylinder itself may rotate.

investigated. The amphiphilic detergent ion which is the principal agent in causing phase formation must have a very restricted diffusion process since the ionic head group is largely confined to residence in the electrical double layer region to preserve the long-range order. Two-dimensional diffusion in the curved surface of the electrical double layer is indicated by the large surface area occupied by ionic head groups.¹⁹ The restricted translational diffusion of the ionic head group $-ND_3^+$ in phase d of this work is reflected in the higher degree of orientation in this component of the lyotropic nematic phase.

The paper of Rowell, Phillips, Melby, and Panar²¹ reports an investigation of the degree of orientation in the thermotropic nematic phases of 4,4'-azoxydianisole, 4,4'-azoxydiphenetole, and 4-(*n*-propyloxy)benzoic acid. By studying both the proton and deuterium magnetic resonance spectra of specifically deuterated derivatives in side chain and ring protons, the microdegree of order of the molecule was related to the macroscopic degree of order of the nematic medium. The molecules tend to line up parallel to the applied magnetic field within a 10° oscillation angle, either side of this axis, and have freedom of rotation within the molecule as well as rotational freedom about other axes in the side chains. Conceptually the discussion of the microdegree of orientation in lyotropic nematic phases and its translation into the macrodegrees of order measured by other techniques is more difficult. The detergent molecule ions are, in the middle phase, ac-

(21) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

ording to X-ray diffraction measurements, arranged with polar groups on the surface of a cylinder, and the interior of the cylinder contains poorly crystallized hydrocarbon chains.³ The uniaxial cylindrical superstructure is coincidental with the optic axis in macroscopically ordered samples.¹⁸ The two-dimensional diffusion of ionic head groups in the cylindrical surface is probably facile while restricting the ionic group to a macroscopically static electrical double layer.

The deuterium quadrupole coupling measured here for the ionic head group $-ND_3^+$ and adjacent $-CD_2-$ provides valuable information. A microdegree of order for the whole decyl chain is not meaningful in the lyotropic phase since this presumably changes from the head group to the end of the chain as freedom of motion comes for each successive $-CH_2-$ group increase in angle. The $-ND_3^+$ and $-CH_2-$ groups in the 1,1,1,2,2-pentadeuteriododecylammonium ion define axes for the N-D and C-D bonds which may have only one type of relative motion to one another, namely rotation about the C-N bond.

The molecular model of the ionic head group region depicted in Figure 3a is useful in developing the following discussion of the degree of orientations measured experimentally. Consider an axis z which is perpendicular to the average interface of the electrical double layer. If the decylammonium ion has its chain fully extended in all trans conformations and the chain is immobile, then the axis z will be along the chain axis bisecting the C-C bonds and making an angle γ with these bonds. The $-CD_2-$ methylene groups define a "DCD" plane perpendicular to the chain axis. The various chain axis segments because of local motions will of course deviate from the x directions in a random oscillatory manner. The angle CND in the head group is designated as ϕ . The motions of the two groups $-CD_2-$ and $-ND_3^+$ can be classified according to (a) internal and macroscopic rotational motions, (b) conformational averaging motions, and (c) oscillation of the whole chain about the z axis. Each of these contributes to the microdegree of orientation of the detergent ion segments. In the present study the degree of orientation of the ionic head group $-ND_3^+$ must be related to the adjacent $-CD_2-$ group directly since the two groups are joined by a common C-N bond. The ratio of the partially averaged quadrupolar splittings for these two sets of deuterium nuclei is close to 2.4 over a 13° temperature range.

Referring to Figure 3a, the degree of orientation of the chain axis "zz," which at the head group is the approximate bisector of the penultimate "C-N" bond, can be written in terms of the angles γ and ϕ and the degree of orientation S_{zz} of this segment of the chain. S_{zz} encompasses any oscillatory movement about the fixed space axis z of the chain segment and thus an expression for S_{ND} , the degree of orientation of the N-D bond, becomes

$$S_{ND} = 1/2(3 \cos^2 \phi - 1)1/2(3 \cos^2 \gamma - 1)S_{zz}^N \quad (5)$$

The superscript on S_{zz}^N denotes a value derived from the N-D axis.

In the case of an array of cylindrical superstructures with the head groups on the surface, the segment's axis "zz" has the possibility of a diffusional motion around the axis of the cylinders and also follows the rotational

and diffusional properties of the cylinders themselves. The cylinder axes have a degree of orientation which tend toward a value $-1/2$, being perpendicular to the magnetic field. Consequently, the chain segment axis "zz" or the space fixed axis "z" can be considered to average over a circle which has a diameter in the magnetic field direction as illustrated in Figure 3c. Assuming that $\phi = 110.5^\circ$ as in the methylammonium ion,^{8b} then $1/2(3 \cos^2 \phi - 1) = -0.3160$. Taking the NCC angle as 112° , then $\gamma = 34^\circ$ and $1/2(3 \cos^2 \gamma - 1) = 0.5310$. For a tetrahedral NCC angle, $1/2(3 \cos^2 \gamma - 1) = 0.5000$.

The experimental degree of orientation of the N-D bond is obtained from the quadrupole splitting of 7.3 kHz at 24.5° (Table II) according to eq 4 cited earlier. The value of Q_{ND} for the methylammonium ion is 176.7 kHz.^{8a} Using this value, $S_{ND} = \pm 0.02754$ and is the microdegree of orientation of the N-D bond. A corresponding computation of the microdegree of orientation along the C-D bond adjacent to the head group assumes $Q_{CD} = 170.0$ kHz and uses the value $\Delta\nu_{Q_{CD}} = 17.4$ kHz from Table II at 24.5° . The degree of orientation obtained is ± 0.06824 (S_{CD}).

Equation 5 may be used to compute S_{zz} , the degree of orientation of the chain axis segment at the two head groups. From eq 5 upon substituting $\phi = 110.5^\circ$ and $\gamma = 34.0^\circ$, we have eq 6. From the value $S_{ND} =$

$$S_{ND} = -0.1678S_{zz}^N \quad (6)$$

± 0.02754 we obtain $S_{zz}^N = \pm 0.1641$. The contribution to the microdegree of orientation from diffusion of chains around the cylinders (Figure 3c) or from rotation of the cylinders themselves is a factor $1/2(3 \cos^2 \alpha - 1)$ where α ranges from 0 to 360° and the angular brackets indicate an average value. Extracting this macroscopic rotational-diffusion contribution (a factor of 0.25) the value $S_{zz}^N = +0.6565$ is obtained. The absolute positive sign can now be assigned because $S_{zz}^N > 0.5$. The value S_{zz}^N is the degree of orientation of the chain axis segment at the $-CD_2ND_3^+$ group with respect to the fixed space axis z which is assumed to lie along the magnetic field axis (Figure 3a) after rotation of the chain segment about the cylinders has been taken into account.

Because of conformational possibilities different from that of the $-ND_3^+$ group, the degree of orientation of the chain segment axis obtained from the $-CD_2-$ group may be different from that of the $-ND_3^+$ group. The value $S_{CD} = \pm 0.06824$ can be computed in terms of the segment axes S_{zz}^C by eq 7 which is equivalent to eq 5 for

$$S_{CD} = 1/2(3 \cos^2 \beta - 1)S_{zz}^C \quad (7)$$

the $-ND_3^+$ group. Since the angle β between the C-D bond and the chain segment axis is 90° (Figure 3a), then S_{zz}^C becomes ± 0.1365 where the superscript indicates a value obtained from the experimental C-D quadrupolar splitting axis. Taking into account the rotation of the segment around the cylindrical superstructure as for the $-ND_3^+$ group, the value S_{zz}^C is $+0.5459$. The prime denotes a degree of orientation with respect to the fixed space axis z or magnetic field axis. Again we have a positive sign since $|S_{zz}^C| > 0.5$.

If there is no relative motion between the $-ND_3^+$ and the $-CD_2-$ groups, the ratio S_{zz}^C/S_{zz}^N is 1, but the experimental value is 0.8315. From this it is evident that

the $-CD_2-$ group has additional averaging motions to the $-ND_3^+$ group. The additional relative motion of the $-CD_2-$ group is consistent with the conformational changes depicted in Figure 3b. The $-ND_3^+$ group can be in either of two gauche conformations with respect to the second carbon from the head group (Figure 3b I or II). In I the $-ND_3^+$ group is rearranged with respect to the original chain axis z while in II the second carbon atom is rearranged with respect to the original chain axis. The ratio 0.8315 for the degrees of orientation of the chain segment axis S_{zz}^C/S_{zz}^N indicates a preponderance of conformational change between the conformations in Figure 3a and 3b II. If we assume that a negligible amount of conformer depicted in Figure 3b I is present, then the degree of orientation of the C-D axis can be written

$$S_{CD} = -0.5S_{zz} + (1 - x)(-0.01)S_{zz} \quad (8)$$

where S_{zz} refers to the degree of orientation of the chain segment axis ($-CD_2ND_3^+$), taking into account a fractional population "x" in the form of Figure 3a and $(1 - x)$ in the form of Figure 3b II. The factor -0.01 is derived from one C-D bond remaining perpendicular to the zz segment axis and the other changing to an angle ξ to this axis as depicted in Figure 3b II. For the conformation in Figure 3b II alone, the degree of orientation can be written as (9). Since ξ is near 36° , then $S_{CD}' \sim -0.01S_{zz}'$, the value of which has been substituted into eq 8.

$$S_{CD}' = 1/2[1/2(3 \cos^2 90 - 1) + 1/2(3 \cos^2 \xi - 1)]S_{zz} \quad (9)$$

A similar equation to (8) can be written for the degree of orientation of the N-D bond, but this value is not affected so we have

$$S_{ND} = -0.1678S_{zz} \quad (10)$$

From (8) and (10) we can write the fraction

$$\frac{S_{ND}}{S_{CD}} = \frac{-0.1678S_{zz}}{-0.5xS_{zz} + (1 - x)(-0.01)S_{zz}} \quad (11)$$

Since the ratios of quadrupolar splittings (Table II) appear to be constant over a 13° temperature range, it is better to use the average value of S_{ND}/S_{CD} in eq 11. From this we find that $x = 0.83$. Thus approximately 83% of the chains are in the extended conformation at least at the $-CD_2ND_3^+$ group.

Expressing this conformational equilibrium in terms of energy we have (12) where k is the equilibrium con-

$$k = \exp(\Delta H/RT) \quad (12)$$

stant for the conformation process and ΔH is the energy difference between the forms represented by Figures 3a and 3b II. Using T equal to 31° , we obtain a ΔH of -960 cal mol⁻¹. It is now clear that a temperature range of 13° will affect the equilibrium only very slightly and thus one would not expect to see a change in ratios of quadrupolar splittings, at least to the accuracy we are measuring them.

A ΔH of 960 cal mol⁻¹ is a very reasonable figure considering that the rotation depicted in Figure 3b II involves either sweeping out a very large volume as the hydrocarbon chain is displaced or the formation of a gauche rotamer which decreases substantially the

volume necessary at the cost of the interaction energy for the second rotamer. For a normal hydrocarbon a gauche rotamer is about $0.5 \text{ kcal mol}^{-1}$ above that for a trans rotamer.²² The value we observe could indicate an increased rigidity of a hydrocarbon chain when it is packed in a liquid crystal. Results somewhat similar to these have been obtained in a more indirect manner from spin label work, particularly that of Seelig and his coworkers.^{23,24}

Conclusion

In this study we have examined some of the properties of the model membrane system based on decylammonium chloride. Proton nuclear magnetic resonance in conjunction with the anisotropic properties of the middle soap region of this cationic surfactant has enabled us to determine the carbon and hydrogen positions in the acetate ion. These structural data in conjunction with the deuterium nmr spectrum from the

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fully deuterated ion were then used to determine the quadrupole coupling constant for the deuteriums of the perdeuteriomethyl group of the ion.

Deuterium magnetic resonance studies of the specifically deuterated 1,1,1,2,2-pentadeuteriodecylammonium ion were able to describe the microdegrees of order of the headgroups in the electrical double layer. The motions of the headgroups are considerably restricted and can be accounted for in terms of oscillations of the segment axis of the $-\text{CD}_2\text{ND}_3^+$ group, rotation of the $-\text{ND}_3^+$ group, and finally rotations about the C-N bond which probably involve gauche conformers in the hydrocarbon chain.

Assuming the superstructure of the phase to be of the cylindrical type, the lateral diffusion of the detergent ions or rotation of the cylinders themselves can be accounted for in the experimental degrees of orientation. The methodology developed for treating this system can be generalized to other systems and has the advantage that unlike results obtained from spin labels there is unlikely to be any perturbation of the system under study. Application of this technique to other model membrane systems whether of lamellar or cylindrical type can therefore be expected to be particularly rewarding.

Low-Pressure Gas-Phase Ozone-Olefin Reactions. Chemiluminescence, Kinetics, and Mechanisms

B. J. Finlayson, J. N. Pitts, Jr.,* and R. Atkinson

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Abstract: Chemiluminescence from $\text{HCHO}(^1\text{A}'' \rightarrow ^1\text{A}_1)$, $\text{OH}(X^2\pi_i)_{v' \leq 9}$, and $\text{OH}(A^2\Sigma^+)$ has been observed in the gas-phase reactions of 2% O_3 in O_2 , N_2 , or He with a series of simple olefins in a flow system at room temperature and at total pressures of 2–10 Torr. The vibration-rotation emission from $\text{OH}(X^2\pi_i)_{v' \leq 9}$ was virtually identical with OH Meinel band emission from reaction $2, \text{H} + \text{O}_3 \rightarrow \text{OH}(^2\pi_i)_{v' \leq 9} + \text{O}_2$, confirming that H atoms are formed in O_3 -olefin reactions under these experimental conditions. In the presence of O_2 , glyoxal phosphorescence was identified in the 2-butene (cis or trans) reaction and methylglyoxal phosphorescence was tentatively identified from the reactions of isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene with ozone. The number of quanta emitted per molecule of reactant consumed at 4.6 Torr total pressure in the ethylene and cis-2-butene reactions was estimated to be 10^{-7} for $\text{HCHO}(^1\text{A}'' \rightarrow ^1\text{A}_1)$ and 10^{-5} quanta for $(\text{CHO})_2(^3\text{A}_u \rightarrow ^1\text{A}_g)$ in the cis-2-butene reaction. Approximately 10^{-7} quanta were emitted in the (9,3) transition of vibrationally excited OH per molecule of reactant consumed, indicating that the formation of vibrationally excited OH is a surprisingly efficient process under these conditions. In the ethylene, cis-2-butene, and isobutene reactions, the time decay of light emission from each excited species was exponential in O_2 but nonexponential in N_2 or He, with increased emission intensities occurring at reaction times $\lesssim 0.1$ sec in the latter case. Rate constants, determined from the loss of O_3 in both O_2 and N_2 as diluents, assuming 1:1 stoichiometry, were a factor of 2–5 times greater in N_2 . In 10 Torr of O_2 , the measured rate constants for the ethylene, cis-2-butene, and isobutene reactions respectively were $1 \pm 1 \times 10^3$, $6.3 \pm 1.9 \times 10^4$, and $5.4 \pm 2.3 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$. Major products of the reaction of cis-2-butene with ozone in either O_2 or N_2 as the carrier gas were, in addition to acetaldehyde, 2-butanone, possibly from the OH-cis-2-butene reaction, and methyl vinyl ketone which was observed only in oxygen. The results are discussed in terms of the O'Neal-Blumstein theory of gas phase ozone-olefin reactions and the possible role of these reactions in photochemical smog formation is considered.

Extensive mechanistic investigations of the liquid-phase reactions of ozone with olefins have identified many of the reaction intermediates and have established the Criegee zwitterion mechanism as a major reaction pathway.¹⁻⁴ Until recently, the Criegee mech-

anism has also been widely assumed to apply to the initial steps of the gas-phase reaction. However, in the gas phase at room temperature, unimolecular decom-

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