

# Nonconcerted Cycloreversion by Electron Impact of Substituted 2,4-Azetidinediones. Relations between the Mass Spectral and Photochemical Reactions

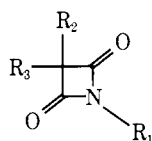
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**Abstract:** The transition state for production of ketene ions and isocyanic acid or isocyanates from the molecular ions of substituted 2,4-azetidinediones (I–VIII) was studied for the metastable reaction occurring in the first field-free region of the mass spectrometer. The effect of 1 and 3 substituents upon the partitioning of the reverse activation energy between translational and internal energy of the reaction products indicates competition between reactions proceeding via primary fissions of the C–CO and N–CO bonds, producing acyclic intermediates a and b, respectively. Formation of ions a, which possibly rearrange to a five-membered cyclic structure c prior to decomposition, is enhanced by 3-phenyl and 3-isopropyl substituents, while a 1-phenyl group promotes production of ions b. The activation energies for the consecutive steps in the reaction of the molecular ions generally very low, i.e., about 0.05–0.1 eV. A 0.9 eV activation energy, found for 1-phenyl-3,3-diethyl-2,4-azetidinedione (VII), is ascribed to the energetically favorable formation of a nonreactive molecular ion, having a resonance stabilized structure b. A striking analogy is found between the mass spectral and photochemical reactions; in the latter, intermediates of type a lead to ring-expansion products, stabilized by the addition of methanol, while intermediates of type b give rise to cycloreversion products.

The photochemical reactions of 2,4-azetidinediones (I to VIII, Scheme I) in methanol recently have been investi-

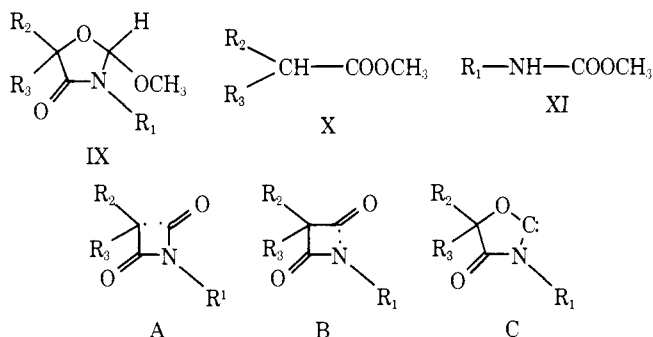
Scheme I. Structures of the 2,4-Azetidinediones Reported



- I,  $R_1 = H$ ;  $R_2 = R_3 = \text{isopropyl}$
- II,  $R_1 = \text{methyl}$ ;  $R_2 = R_3 = \text{isopropyl}$
- III,  $R_1 = 2,2,2\text{-trifluoroethyl}$ ;  $R_2 = R_3 = \text{isopropyl}$
- IV,  $R_1 = H$ ;  $R_2 = R_3 = \text{ethyl}$
- V,  $R_1 = H$ ;  $R_2 = \text{ethyl}$ ;  $R_3 = \text{phenyl}$
- VI,  $R_1 = \text{methyl}$ ;  $R_2 = \text{ethyl}$ ;  $R_3 = \text{phenyl}$
- VII,  $R_1 = \text{phenyl}$ ;  $R_2 = R_3 = \text{ethyl}$
- VIII,  $R_1 = R_2 = R_3 = \text{phenyl}$

gated in our laboratory.<sup>1</sup> On the basis of <sup>13</sup>C NMR evidence<sup>1</sup> and a detailed investigation of the mass spectra,<sup>2</sup> 2-methoxy-4-oxazolidone structures (IX) (Scheme II) have

Scheme II. Reaction Products and Intermediates Formed in the Photolysis of Compounds (I to VIII) in Methanol Solution<sup>1,2</sup>



been assigned to the photocycloexpansion products obtained in these reactions. Concurrently with IX products X and XI are produced by addition of methanol to the primary cycloreversion products, i.e., derivatives of ketene and isocyanic acid. The relative yields of product IX and products X and XI depend on the nature of the substituents  $R_1$ ,  $R_2$ , and  $R_3$ .

We decided to investigate the relations between the photochemical reactions of 2,4-azetidinediones and the reactions induced by electron impact. Diradical intermediates A and B have been postulated<sup>1</sup> as intermediates in order to account for the products of photocycloexpansion and photocycloreversion, respectively. Only cycloreversion can be observed in the unimolecular gas phase fragmentations of ionized 2,4-azetidinediones, producing ketene ions and isocyanic acid or isocyanates  $R_1\text{NCO}$ . If acyclic radical ions analogous to the diradical intermediates A and B are formed by electron impact, they cannot be trapped by secondary reaction with other molecules; hence both type A and B intermediates could give rise to cycloreversion.

Recent results of Cooks et al.<sup>3</sup> indicate that transition states of metastable reactions in the mass spectrometer can be characterized by measuring the fraction of the reverse activation energy ( $\epsilon_0'$ ) that is released as translational energy ( $T^\circ$ ) of the reaction products. High and low values for the energy partitioning quotient  $T^\circ/\epsilon_0'$  would correlate respectively with "tight" and "loose" activated complexes. Since, for instance, three- and four-membered cyclic transition states would be tight and acyclic transition states would be loose, it should be possible to distinguish between a concerted and stepwise reaction of the ionized 2,4-azetidinediones.

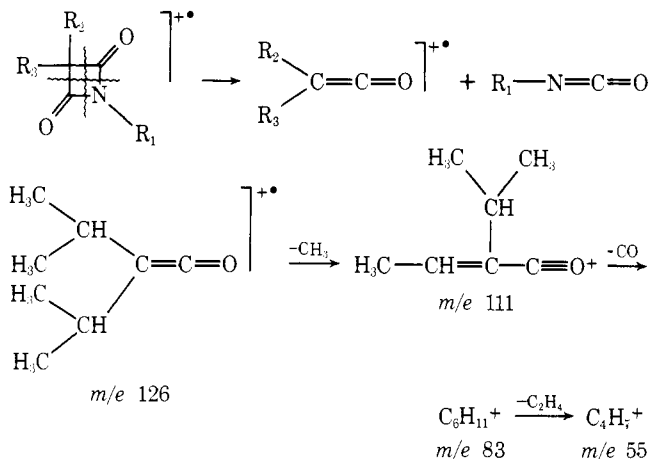
## Results

**Mass Spectra of 2,4-Azetidinediones (I to VIII).** The 70-eV spectra are listed in Table I. Ring cleavage with formation of a ketene fragment ion constitutes the most prominent fragmentation pathway in the spectra of azetidinediones (I to VIII). Fission of either 1,2 and 3,4 or 2,3 and 1,4 bonds could generate the ketene species (Scheme III). The direction of charge retention relates to the higher ionization potentials for  $\text{HNCO}$ ,  $\text{CH}_3\text{NCO}$ , and  $\text{C}_6\text{H}_5\text{NCO}$  (11.6,<sup>4a</sup> 10.7,<sup>4a</sup> and 9.2 eV,<sup>4b</sup> respectively) as compared to the IP for the substituted ketenes (7.85–8.24 eV, Table III).

Similar correlations were observed for the ring cleavage reaction in cyclobutanones: in the mass spectrum of cyclobutanone<sup>5</sup> the charge remains mainly with the ketene fragment (IP ketene 9.6 eV and IP ethylene 10.5 eV) while for 2-methyl and 2,2-dimethyl substituted cyclobutanones<sup>5a</sup> the alkylene fragment (IP propylene 9.7 eV and IP isobutylene

Table I. 70 eV Mass Spectra of Azetidinediones I–VIII

3,3-Diisopropyl-2,4-azetidinedione (I)	39 (9), 40 (2), 41 (20), 42 (1), 43 (9), 51 (1), 53 (3), 55 (37), 56 (2), 67 (3), 68 (1), 69 (1), 83 (40), 84 (3), 111 (100), 112 (7), 126 (65), 127 (6), 169 (1.0)
1-Methyl-3,3-diisopropyl-2,4-azetidinedione (II)	39 (7), 40 (4), 41 (10), 42 (3), 43 (4), 44 (3), 53 (2), 55 (15), 56 (1), 67 (2), 83 (40), 84 (2), 111 (100), 112 (7), 126 (71), 127 (6), 183 (0.7)
1-(2,2,2-Trifluoroethyl)-3,3-diisopropyl-2,4-azetidinedione (III)	39 (6), 40 (1), 41 (10), 43 (8), 53 (2), 55 (20), 56 (3), 67 (2), 68 (1), 69 (1), 83 (25), 84 (1), 111 (100), 112 (7), 125 (1), 126 (88), 127 (7), 162 (2), 204 (2), 251 (0.35)
3,3-Diethyl-2,4-azetidinedione (IV)	39 (23), 40 (3), 41 (23), 42 (10), 43 (3), 44 (1), 51 (2), 53 (6), 54 (3), 55 (95), 56 (4), 67 (1), 69 (3), 70 (4), 83 (100), 84 (5), 98 (90), 99 (6), 141 (1.4)
3-Ethyl-3-phenyl-2,4-azetidinedione (V)	39 (8), 41 (3), 43 (3), 50 (4), 51 (13), 51.5 (6), 52 (4), 57 (1), 57.5 (3), 58 (4), 62 (2), 63 (5), 65 (3), 65.5 (2), 77 (10), 78 (5), 89 (6), 91 (12), 102 (3), 103 (25), 104 (3), 115 (12), 116 (6), 117 (65), 118 (27), 119 (2), 131 (2), 146 (100), 147 (9), 189 (1.2)
1-Methyl-3-ethyl-3-phenyl-2,4-azetidinedione (VI)	39 (3), 43 (4), 50 (1), 51 (4), 51.5 (1), 52 (1), 58 (4), 62 (1), 63 (2), 65 (1.5), 77 (4), 78 (2), 89 (3), 91 (6), 102 (1), 103 (11), 104 (1), 115 (5), 116 (3), 117 (25), 118 (14), 119 (1), 131 (2), 146 (100), 147 (10), 203 (0.3)
1-Phenyl-3,3-diethyl-2,4-azetidinedione (VII)	39 (7), 40 (1), 41 (10), 42 (3), 51 (2), 53 (2), 55 (25), 56 (1), 63 (1), 64 (2), 65 (1), 69 (2), 70 (2), 77 (4), 83 (60), 84 (3), 91 (5), 98 (100), 99 (7), 119 (8), 132 (4), 217 (39), 218 (5)
1,3,3-Triphenyl-2,4-azetidinedione (VIII)	51 (3), 63 (3), 64 (2), 77 (4), 89 (2), 91 (5), 115 (4), 119 (3), 139 (4), 163 (4), 164 (5), 165 (68), 166 (58), 167 (7), 194 (100), 195 (15), 196 (1), 256 (0.7), 313 (0.30)

Scheme III. Production of Ketene Ions and Isocyanic Acid or Isocyanates from the Diones (I to VIII)<sup>a</sup>

<sup>a</sup> The further decomposition of the diisopropylketene ion generated from I to III is illustrated.

9.2 eV) carries an increasing portion of the total ion current.

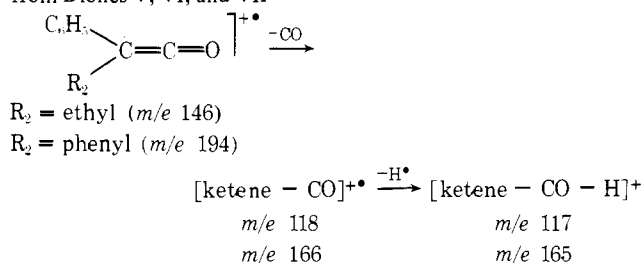
The same type of ring cleavage occurs also in the mass spectra of cyclobutanes,<sup>6</sup> 1,3-cyclobutanediones,<sup>7</sup> azetidines,<sup>8,9</sup> and 2-azetidines.<sup>9-12</sup>

Scheme III illustrates the further fragmentation of the ketene ion *m/e* 126 produced from diones I to III. Consecutive losses of CH<sub>3</sub>, CO, and C<sub>2</sub>H<sub>4</sub> are supported by the appropriate metastable ions and by precise mass measurements. Loss of an isopropyl group from the ketene ion *m/e* 126, yielding an ion *m/e* 83 with composition C<sub>5</sub>H<sub>7</sub>O, contributes to a very small extent only.

The phenylethylketene and diphenylketene ions produced from diones V, VI, and VIII respectively mainly react by

consecutive losses of CO and one hydrogen atom (Scheme IV). High resolution measurements performed for V, also

Scheme IV. Consecutive Losses of CO and H from Phenylethylketene and Diphenylketene Ions Generated from Diones V, VI, and VII



revealed small contributions of [ketene-C<sub>2</sub>H<sub>4</sub>]<sup>+</sup> ions to *m/e* 118 and [C<sub>8</sub>H<sub>7</sub>N]<sup>+</sup> ions to *m/e* 117.

Table II lists the relative intensities of molecular ions, ketene ions, and ketene fragment ions at 70, 15, and 10 eV. Weak relative intensities (0.3–1.4%) are observed for the molecular ions in the 70 eV spectra of diones I to VI and VIII. Their relative intensities do not increase appreciably at low electron energies.

The mass spectrum of VII deviates considerably from this general trend. The relative intensity of the molecular ion amounts to 39% at 70 eV and 75% at 15 eV; in the 10 eV spectrum it carries 80% of the total ion current.

The rate of the secondary expulsion of a methyl group from the dialkylketene ions, expressed as the intensity ratio [ketene-CH<sub>3</sub>]<sup>+</sup>/[ketene]<sup>+</sup>, shows a marked decrease with increasing size of the 1-substituent. The effect appears from the 70 and 15 eV intensity data (Table II) for the diisopropylketene ion produced from I, II, and III and for the diethylketene ion generated from IV and VII. Partitioning of excess internal energy between the fragments formed in the primary cycloreversion process results in decreasing energy available for secondary decomposition of the ketene ion with increasing size of the neutral lost. This “degrees of freedom” effect<sup>13</sup> was observed first for secondary (metastable) fragmentation of [C<sub>3</sub>H<sub>6</sub>O]<sup>+</sup> produced from a series of homologous 2-alkanones.<sup>14</sup>

**The Ketene Ions.** In order to gain insight into the mechanism of ketene ion formation from azetidinediones I to VIII, we investigated the excess energy involved in the formation of the reaction products and the fraction of it released as kinetic energy. According to Cooks et al.<sup>3</sup> the translational energy *T*, measured from the metastable peak width, arises by partitioning of (i) the excess internal energy of the activated complex (ε<sup>‡</sup>) and (ii) the reverse activation energy (ε<sub>0</sub><sup>r</sup>) between translational and internal energy of the reaction products

$$\epsilon_{\text{excess}} = \epsilon^{\ddagger} + \epsilon_0^r$$

and

$$T = T^{\ddagger} + T^e$$

where ε<sup>‡</sup> → *T*<sup>‡</sup> and ε<sub>0</sub><sup>r</sup> → *T*<sup>e</sup>.

Since ε<sup>‡</sup> tends to be partitioned in a statistical manner among the number of oscillators of the molecule,<sup>3,15</sup> only a small fraction of it will be released as kinetic energy *T*<sup>‡</sup> for large molecules. On the contrary the quotient *T*<sup>e</sup>/ε<sub>0</sub><sup>r</sup> would be characteristic of the transition state, being high for tight activated complexes and low for loose activated complexes.

The excess energy term ε<sub>excess</sub> was determined from eq 1.

$$\begin{aligned} \text{AP}(\text{ketene}^{*}) &= \Delta H_f(\text{ketene}^{*}) + \\ &\quad \Delta H_f(\text{R}_1\text{NCO}) - \Delta H_f(\text{I to VIII}) + \epsilon_{\text{excess}} \\ \text{IP}(\text{ketene}) &= \Delta H_f(\text{ketene}^{*}) - \Delta H_f(\text{ketene}) \quad (1) \\ \text{AP}(\text{ketene}^{*}) - \text{IP}(\text{ketene}) &= \Delta H_f(\text{ketene}) + \\ &\quad \Delta H_f(\text{R}_1\text{NCO}) - \Delta H_f(\text{I to VIII}) + \epsilon_{\text{excess}} \end{aligned}$$

Table II. Relative Intensities of Molecular Ions, Ketene Ions, [Ketene-CH<sub>3</sub>]<sup>+</sup>, [Ketene-CO]<sup>+</sup>, and [Ketene-CO-H]<sup>+</sup> Ions in the Mass Spectra of Azetidinediones I to VIII at 70, 15, and 10 eV

Compd	<i>m/e</i>	Molecular ion			[Ketene] <sup>+</sup>				[Ketene-CH <sub>3</sub> ] <sup>+</sup>				[Ketene-CO] <sup>+</sup> and [ketene-CO-H] <sup>+</sup>			
		Intensity, eV			Intensity, eV				Intensity, eV				Intensity, eV			
		70	15	10	<i>m/e</i>	70	15	10	<i>m/e</i>	70	15	10	<i>m/e</i>	70	15	10
I	169	1.0	1.3	0.8	126	65	100	100	111	100	83	2				
II	183	0.7	0.7	2	126	71	100	100	111	100	66	2				
III	251	0.35	0.35	0.4	126	88	100	100	111	100	40	1				
IV	141	1.4	1.1	3	98	90	100	100	83	100	60	2				
V	189	1.2	1.2	3	146	100	100	100					118	27	8	1.6
													117	65	6	3
VI	203	0.30	0.60	1	146	100	100	100					118	14	4	
													117	25	2	
VII	217	39	75	100	98	100	100	16	83	60	11	4				
VIII	313	0.30	0.25	2	194	100	100	100					166	58	8	10
													165	68	0.4	

Table III. Energetics of Ketene Ion Formation from Azetidinediones I to VIII<sup>a</sup>

Compd	<i>T</i> <sup>b,c</sup>	IP <sup>d</sup> (I to VIII)	AP <sup>d</sup>		IP <sup>d</sup> (ketene)	Δ <i>H</i> <sub>f</sub> <sup>o</sup>			ε <sub>excess</sub> (m*) <sup>f</sup>	<i>T</i> /ε <sub>excess</sub> (m*) <sup>f</sup>
			(ion source ketene ion)	(metastable ketene ion)		I to VIII <sup>e</sup>	Ketene <sup>e</sup>	R <sub>1</sub> NCO <sup>e</sup>		
I	0.038	9.42	9.64	9.49	8.09	-4.03	-2.11	-1.08	0.56	0.07
II	0.005	9.27	9.68	9.39	8.09	-3.92	-2.11	-1.47	0.96	0.005
III	0.012	9.50	9.68	9.55	8.09	-10.64	-2.11	-8.20	1.13	0.01
IV	0.018	9.57	9.70	9.60	8.24	-3.56	-1.56	-1.08	0.44	0.04
V	0.050	8.90	9.23	8.97	7.94	-1.92	-0.05	-1.08	0.24	0.2
VI	0.006	8.82	9.23	8.83	7.94	-1.81	-0.05	-1.47	0.60	0.01
VII	0.018	8.71	10.26	9.61	8.24	-2.09	-1.56	-0.18	1.02	0.02
VIII	0.012	8.37	8.98	8.46	7.85	1.18	1.65	-0.18	0.32	0.04

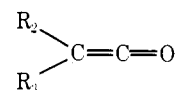
<sup>a</sup> All values in electron volts. <sup>b</sup> Translational energy calculated<sup>3</sup> from metastable peak width at half-height. <sup>c</sup> Metastable ions originating in the first field-free region and refocused at the appropriate ESA potential. <sup>d</sup> Ionization and appearance potentials were measured at ~70° using the semilogarithmic plot method. Distances between the curves for compounds I to VIII and the calibrant (benzene, electron-impact IP 9.50 eV) were determined at 0.1% of the ion current at 50 eV. <sup>e</sup> Standard heats of formation derived as explained in text. <sup>f</sup> Derived from eq 1 by using metastable ion appearance potentials.

The terms in eq 1 represent the appearance potentials (AP) for the ketene fragment ions, the ionization potentials (IP) for the neutral substituted ketenes, and the standard heats of formation for ketenes, for isocyanic acid or isocyanate esters, and for azetidinediones I to VIII.

Table III summarizes the experimental results for ketene ion formation from azetidinediones I to VIII. Rather weak metastable ions, associated with ketene ion formation from the low-intensity molecular ions, are generated in the second field-free region. Refocusing of metastable ions formed between ion source and electrostatic analyzer, however, yields intense signals, suitable for measurement of their AP and peak width. These metastable ions originate only in unimolecular transitions, since their intensity and peak shape are not affected by admitting increasing amounts of collision gas (air, pressure until 10<sup>-5</sup> Torr) in the analyzer region.

The AP for both the ion source and metastable reaction are reported in columns 4 and 5, but only the AP(m\*) has been used in the calculation of ε<sub>excess</sub>(m\*). This procedure has the advantage that the values for AP and *T* are measured on the same signal, avoiding ambiguities due to different time scales for the ion source and metastable reactions. The differences between the AP(m\*) and the IP for I to VIII, except VII, are very small, ranging from 0.03 to 0.12 eV. The very narrow and, hence, very similar energy distribution for the stable and metastable molecular ions results in similar shapes for their ionization efficiency curves. The latter in turn closely resemble that of the calibrant (benzene, electron-impact IP = 9.50 eV). These observations not only justify the normalization procedure used in the semilogarithmic plot method<sup>16</sup> but also give additional support for the use of AP determined for the metastable rather than for the ion source reaction.

The AP for the ion source ketene ions lie 0.1–0.6 eV above the AP for the metastable ketene ions. The ionization efficiency curves showed considerable tailing below 0.2% of the ion current at 50 eV for compounds I, III, IV, V, and VII. This tailing was due to some thermal decomposition in the ion source, operated at 70°, with generation of small amounts of the ketenes



The thermal reaction is shown by the variation of the AP values (taken at 0.1% of the ion current at 50 eV) upon changing the temperature in the heated inlet system and upon replacing the latter by a cooled direct inlet system. The curves for diones II, VI, and VIII show a slight tailing only below 0.1% ion current. This curvature could be due to unresolved low-energy transitions.<sup>17</sup> Interpretation of these curves with the EDD (Energy Distribution Difference)<sup>17–20</sup> technique possibly would yield AP for the ion source ketene ions, which are more in line with the metastable AP. Difficulties associated with thermal decomposition in the ion source, however, are eliminated only when the metastable transition is studied.

The IP for dione VII lies 0.9 eV below the AP for the metastable ketene ion. This difference probably results in a relatively broad energy distribution for the stable molecular ions, and accounts for the high abundance (Table II) since a great number of molecular ions will have insufficient energy to undergo reaction.

The kinetic energy release *T* was measured at half-height of the metastable peak, which was plotted by using the accelerating voltage scan technique with narrow settings of the energy resolving β slit. Most values for *T* listed in Table

III lie in the range 5–18 meV which is common for simple cleavage reactions without significant reverse activation energies.<sup>3</sup> When the neutral lost is HNCO (I, IV, and V),  $T$  lies in the range 18–50 meV. The latter values are believed to be derived mainly from  $\epsilon_0$ <sup>4</sup> on the basis of the following argument. The differences between the AP (metastable ketene ion) and the IP for I, IV, and V are very small, i.e., 0.03–0.07 eV. According to the quasi-equilibrium theory, the activation energy  $\epsilon_0$  is the difference between the true AP, not including the excess internal energy  $\epsilon^\ddagger$ , and the adiabatic IP, characteristic of the ground-state molecular ion. If the measured IP for the azetidinediones are adiabatic, then the energy  $\epsilon$  ( $\epsilon = \epsilon_0 + \epsilon^\ddagger$ ) must be equal to about 0.05 eV, and, evidently,  $\epsilon^\ddagger$  (metastable transition) represents only a fraction of this energy. Vertical ionization will proceed far more efficiently than the adiabatic 0–0 transition but the excess vibrational energy imparted by the former process (see below) will give rise to rapid decomposition in the ion source, especially in view of the extremely low activation energy of the reaction. [The relative intensity of the molecular ions falls off rapidly with increasing ion source temperature, i.e., 70–120°, which is below the temperature range where thermal decomposition becomes appreciable, and even at the lowest electron energies the relative intensity does not increase above a few percent (Table II).] Hence, only molecular ions with very little excess internal energy  $\epsilon^\ddagger$  will reach the first field-free region while molecular ions reaching the detector region will possess still lower internal energy. Further partitioning of the small  $\epsilon^\ddagger$  (metastable reaction) between  $T^\ddagger$  and the other degrees of freedom of the molecule in a statistical manner eventually will give rise to a very small  $T^\ddagger$  value.

Ketenes were prepared by thermal decomposition of the corresponding azetidinediones in the heated inlet system at 220°. Their IP are listed in Table III. Although the ionization efficiency curves showed no evidence for alternative ionization processes in the threshold region, the reported values clearly represent vertical ionization processes and must be regarded as upper limits. For ketene the spectroscopic IP (9.61 eV)<sup>21</sup> lies 0.38 eV below the electron-impact IP (9.99<sup>22</sup> eV). The excess energy contained in the electron-impact IP for the dialkylketenes reported probably does not exceed 0.2 eV. Indeed, the difference 1.37 eV between the spectroscopic IP for ketene and our reported IP for diethylketene has a magnitude comparable to the corresponding differences in the photoionization potentials<sup>23</sup> for CH<sub>2</sub>O and Et<sub>2</sub>CO (10.88 eV – 9.32 eV = 1.56 eV) and for CH<sub>2</sub>=CH<sub>2</sub> and EtMeC=CH<sub>2</sub> (10.50 eV – 9.12 eV = 1.38 eV).

Evaluation of eq 1 only requires the difference of the AP (metastable ketene ion) and the IP(ketene), where both values refer to the same calibrant. However, a small error will originate from the difference in ion source temperature (70°) and temperature (25°) to which refer the standard heats of formation of azetidinediones, ketenes, and isocyanic acid or isocyanates.

Both possible errors discussed here will tend to decrease the difference of AP(metastable ketene ion) and IP(ketene) and hence will result in too low values for  $\epsilon_{\text{excess}}(m^*)$  calculated from eq 1.

The heats of formation of azetidinediones I to VIII were calculated by addition of the group contributions to  $\Delta H_f^\circ$ , as given in a review of Benson et al.<sup>24</sup> The relevant group increments are known with sufficient accuracy, except for the group C(CO)<sub>2</sub>(C)<sub>2</sub>. The contribution of the latter group was estimated from the difference ( $\Delta H_f^\circ(\text{C}(\text{CO})(\text{C})_3) - \Delta H_f^\circ(\text{C}(\text{C})_4) = 1 \text{ kcal mol}^{-1}$ ). Ring strain depends primarily on ring size and not significantly on whether a CH<sub>2</sub> has been replaced by an O or an NH group.<sup>24</sup> Accordingly,

Benson et al. proposed a value of 26.2 kcal mol<sup>-1</sup> for the ring strain in azetidines, which is equal to the strain in cyclobutane and oxetane. We assumed the same value for azetidinediones I to VIII, especially in view of two observations: (i) the ring strain for succinimide (8.5 kcal mol<sup>-1</sup>),<sup>24</sup> calculated by using the group increments mentioned before, is only slightly higher than for other five-membered ring systems (6.3 kcal mol<sup>-1</sup>);<sup>24</sup> and (ii) the ring strain for cyclopentanone and cyclobutanone is 1.1 and 4.0 kcal mol<sup>-1</sup> lower than for cyclopentane and cyclobutane, respectively.<sup>25</sup> Hence, relief of torsional strain by introduction of CO groups would be compensated by 1,3-dipolar repulsion.

The  $\Delta H_f^\circ$  values for I to VIII listed in Table III also take into account the presence of eight gauche interactions for the isopropyl groups in I, II, and III and of four gauche interactions for the ethyl groups in IV and VII. Each gauche interaction involves a correction<sup>24</sup> of 0.8 kcal mol<sup>-1</sup>. Gauche and ortho interactions (ortho correction<sup>24</sup> 0.5 kcal mol<sup>-1</sup>) for the 3-phenyl and 3-ethyl groups in V and VI are accounted for by a correction of 4 kcal mol<sup>-1</sup>. Corrections for ortho interactions and other strain in the 3,3-diphenyl compound VIII amount to 5 kcal mol<sup>-1</sup>.

The enthalpy of formation for gaseous ketene ( $-11.4 \pm 0.4 \text{ kcal mol}^{-1}$ ) has been determined recently.<sup>26</sup> Addition of the increments for alkyl and phenyl groups yields the  $\Delta H_f^\circ$  for the substituted ketenes. The procedure applied assumes equivalent contributions for substituents on C=C=O and C=C=C moieties. An analogous assumption for the C=C=C group yields correct results for the heats of formation for alkyl-substituted allenes.<sup>24</sup> The polarity of ketenes is similar to that of olefins and allenes, as shown by the very small dipole moment for ketenes as compared to ketones and especially  $\alpha,\beta$ -unsaturated ketones.<sup>27</sup> Hence, no appreciable error is introduced in the calculation of  $\Delta H_f^\circ$  for alkyl-substituted ketenes. The conjugation energy in phenyl-substituted ketenes is unknown, but probably does not exceed the conjugation energy for styrene (1.7 kcal mol<sup>-1</sup>),<sup>24</sup> implied in the group additivity calculation.

Gauche and ortho interactions in the substituted ketenes are much relieved as compared to the corresponding azetidinediones. Thus for diisopropyl ketone there are only four gauche interactions along a C(sp<sup>3</sup>)-C(sp<sup>2</sup>) bond (correction<sup>24</sup> 0.5 kcal mol<sup>-1</sup>) instead of eight gauche interactions along a C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bond (correction 0.8 kcal mol<sup>-1</sup>). Confirmation for the magnitude of these corrections is obtained by reference to the known<sup>24</sup>  $\Delta H_f^\circ$  for the corresponding ketones R<sub>2</sub>R<sub>3</sub>CO, which show a constant difference with the  $\Delta H_f^\circ$  calculated for ketenes R<sub>2</sub>R<sub>3</sub>C=C=O.

The heat of formation for isocyanic acid ( $-25 \pm 3 \text{ kcal mol}^{-1}$ ) was based<sup>28</sup> on the difference in AP for the ion (NH)<sup>+</sup>• produced from HNCO and HN<sub>3</sub>, and on the AP and kinetic energy release for the metastable transition (HNCO<sup>+</sup>• → HCO<sup>+</sup> + N). This value is in good agreement with an estimated value ( $-27.9 \text{ kcal mol}^{-1}$ )<sup>29</sup> and with a value ( $-24 \pm 3 \text{ kcal mol}^{-1}$ ) determined<sup>30</sup> by photodissociation of HNCO.

The enthalpy of formation for gaseous phenyl isocyanate ( $-4.1 \text{ kcal mol}^{-1}$ ) was calculated from a recently reported heat of combustion (813.2 kcal mol<sup>-1</sup>)<sup>31</sup> and from the heat of vaporization (11.9 kcal mol<sup>-1</sup>) estimated<sup>24</sup> from the boiling point (162–163° (751 mm)).

The  $\Delta H_f^\circ$  tabulated<sup>32</sup> for liquid methyl isocyanate ( $-22.0 \text{ kcal mol}^{-1}$ ) probably is based on a heat of combustion, reported<sup>33</sup> in 1898. Using this value and an estimated heat of vaporization of 10 kcal mol<sup>-1</sup>, Haney and Franklin<sup>34</sup> and Dillard and Franklin<sup>35</sup> studied the electron impact induced reaction [CH<sub>3</sub>NCO<sup>+</sup>• → CH<sub>3</sub><sup>+</sup> + NCO] and obtained apparently consistent results for the heat of formation for the NCO radical and for the partitioning of the ex-

cess excitation energy between internal and translational energy of the reaction products. However, a value  $-12 \text{ kcal mol}^{-1}$  for  $\Delta H_f^\circ(\text{CH}_3\text{NCO}(\text{g}))$  and even a value  $-15 \text{ kcal mol}^{-1}$  ( $\Delta H_{\text{vap}} \sim 7 \text{ kcal mol}^{-1}$  is calculated<sup>24</sup> from the boiling point  $43^\circ$ ) do not fall in line with reported  $\Delta H_f^\circ$  for  $\text{HX}$ ,  $\text{CH}_3\text{X}$ , and  $\text{C}_6\text{H}_5\text{X}$ , where  $\text{X} = \text{NCO}$ ,  $\text{N}_3$  ( $\text{HN}_3$ ,<sup>24,32</sup>  $\text{CH}_3\text{N}_3$ ,<sup>24,36,37</sup>  $\text{C}_6\text{H}_5\text{N}_3$ ,<sup>38</sup>),  $\text{NCS}$  ( $\text{HNCS}$ ,<sup>24,32</sup>  $\text{CH}_3\text{NCS}$ ,<sup>24,32,39</sup>), and  $\text{CN}$ .<sup>24</sup> A consistent  $\Delta H_f^\circ(\text{CH}_3\text{NCO}(\text{g}))$  ( $-34 \text{ kcal mol}^{-1}$ ) is obtained from a recent heat of combustion for hexamethylene diisocyanate ( $1065.7 \text{ kcal mol}^{-1}$ ).<sup>31</sup> With  $\Delta H_{\text{vap}} \sim 15 \text{ kcal mol}^{-1}$  (boiling point  $120\text{--}125^\circ/10 \text{ mm}$ ) this yields  $\Delta H_f^\circ(\text{OCN}(\text{CH}_2)_6\text{NCO}(\text{g})) = -81.6 \text{ kcal mol}^{-1}$ . Application of the group-increment scheme of Benson et al.<sup>24</sup> then leads to the mentioned  $\Delta H_f^\circ$  value.

Estimated errors for the calculated heats of formation for the ketenes, isocyanates, and azetidinediones are in the range  $0.1 \text{ eV}$  and will be mainly systematic for analogous series of compounds. Hence, these errors will affect the absolute magnitude but not the relative order of the energy partitioning quotient  $T/\epsilon_{\text{excess}}(m^*)$ . Actually, the generally small values reported for this quotient (Table III) will tend to be too high, as the difference [AP(metastable ketene ion) – IP(ketene)] could be  $0.2 \text{ eV}$  low. Decreasing the already small values for the quotient  $T/\epsilon_{\text{excess}}(m^*)$  would not change the conclusions reported in the Discussion.

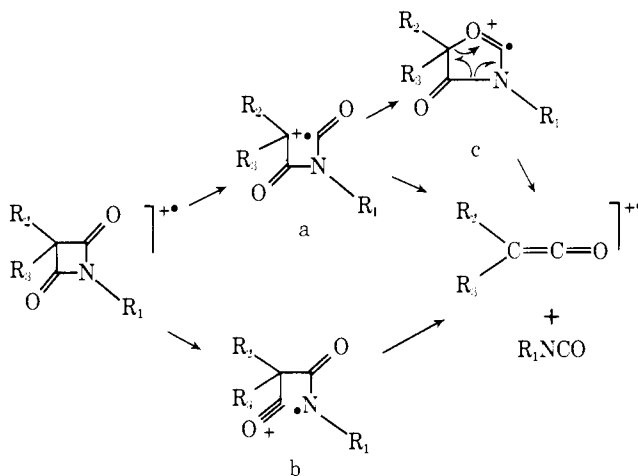
## Discussion

Production of ketene ions and isocyanates from ionized azetidinediones proceeds with a very small activation energy  $\epsilon_0$  (except for VII), but, as  $\epsilon^\ddagger(m^*)$  is small, also with a generally significant reverse activation energy  $\epsilon_0^r$ . The latter result was to be expected since the reaction formally requires cleavage of two bonds and formation of two new bonds. Only for 3-phenyl-substituted diones V and VIII is  $\epsilon_{\text{excess}}(m^*)$  rather small. The fraction of  $\epsilon_{\text{excess}}(m^*)$  released as translational energy is shown by the energy partitioning quotient  $T/\epsilon_{\text{excess}}(m^*)$  listed in the last column of Table III. The values obtained probably represent an upper limit for the quantity of interest  $T^c/\epsilon_0^r$ . Indeed,  $T$  may contain a small contribution  $T^\ddagger$  originating in  $\epsilon^\ddagger$  (metastable ketene ion). Moreover, the values calculated for  $\epsilon_{\text{excess}}(m^*)$  should represent a minimum, as argued in the Results section. A vertical IP for ethylphenylketene exceeding the adiabatic IP with say  $0.2 \text{ eV}$  would result in a twofold decrease in  $T/\epsilon_{\text{excess}}(m^*)$  in the case of dione V, for which the calculated  $\epsilon_{\text{excess}}(m^*)$  is only  $0.24 \text{ eV}$ . It should be noticed, however, that even a value  $0.1$  instead of  $0.2$  for the quotient obtained for V is significantly higher than for the other azetidinediones, except perhaps I. The energy partitioning results allow us to conclude that (i) the quotient is very small for azetidinediones with a substituted nitrogen and (ii) when the neutral molecule lost in the fragmentation is  $\text{HNCO}$ , there is a small but significant increase in  $T/\epsilon_{\text{excess}}(m^*)$  in the series IV, I, and V, having 3,3-diethyl, 3,3-diisopropyl, and 3-ethyl-3-phenyl substituents, respectively. This is also the order of decreasing appearance potentials for ketene ion formation and decreasing dissociation energy for the C–CO bonds in the ionized molecules.

Two different assumptions can explain the latter result. (a) The increase of  $T/\epsilon_{\text{excess}}(m^*)$  in the series IV, I, and V reflects a change from a two-step to a concerted reaction mechanism. The nonconcerted reaction then must involve intermediate b. Lowering the C–CO dissociation energy results in a faster rate for the second reaction step and, hence, in higher  $T$  and  $T/\epsilon_{\text{excess}}(m^*)$  values. (b) Competition occurs between intermediates a and b. The lower C–CO dissociation energy for I and V enhances formation of a. The greater amount of energy released in the reaction coordi-

nate for intermediate a could be due to (i) the partial double bond character of N–CO in a or (ii) rearrangement of a into a five-membered ring structure c, by analogy to the photochemical reaction, followed by decomposition of c into the reaction products (Scheme V).

Scheme V. Acyclic Intermediates a and b Involved in the Cycloreversion of I to VIII<sup>a</sup>



<sup>a</sup> Possible rearrangement of a to c before decomposition into products.

Several observations support the nonconcerted nature of the cycloreversion. First, the low values for  $T$  and  $T/\epsilon_{\text{excess}}(m^*)$  are difficult to reconcile with a four-membered transition state. Loss of  $\text{CH}_2\text{O}$  from substituted anisoles through a four-centered hydrogen transfer yielded  $T \sim 0.3 \text{ eV}$  and  $T/\epsilon_{\text{excess}} \sim 0.2$ .<sup>40</sup> A four-membered transition state was postulated<sup>41</sup> for the metastable elimination of  $\text{HCN}$  from *p*-methoxybenzaloxime *O*-methyl ether on the basis of  $T \sim 0.67 \text{ eV}$  and  $T/\epsilon_{\text{excess}} \sim 0.7$ .

Further evidence disproving a concerted cycloreversion, and more convincing than the absolute magnitude of the energy partitioning quotient, comes from the sharp decrease of  $T$  and  $T/\epsilon_{\text{excess}}(m^*)$  in going from imides I and V to the corresponding *N*-methylimides II and VI. This result implies a very effective transfer of energy by interaction of the degree of freedom represented by the reaction coordinate with the oscillators of the *N*-methyl group. Such energy transfer would be less effective for a tight activated complex, which has a reduced effective number of oscillators.

Consideration of the activation energy for the forward reaction  $\epsilon_0$  sheds some light upon the question, which intermediate, a or b, prevails in the cycloreversion? The 1-phenylazetidinedione (VII) is the only compound which shows an appreciable  $\epsilon_0$  ( $0.9 \text{ eV}$ , Table III) for the metastable reaction. In this case cleavage of the activated N–CO bond could give rise to formation of a substantial portion of “non-reactive” molecular ions having a resonance stabilized structure b. Most “reactive” molecular ions, having enough energy to undergo metastable decomposition, probably do react also via primary N–CO fission. Indeed, as argued before, b is competitive already for the unsubstituted imides I, IV, and V.

In contrast with the high  $\epsilon_0$  found for VII, the very small activation energies for cycloreversion, observed for the molecular ions of I–VI and VIII, suggest the operation of another mechanism.

Indeed, activation of C–CO by 3-phenyl and 3-alkyl substituents and nonactivation of N–CO by the absence of a 1-phenyl group should enhance formation of a for diones I–VI as compared to VII. The small  $\epsilon_0$  values imply that the activation energy for secondary fission of N–CO in a re-

Table IV. Quantum Yield and Yields<sup>a</sup> of Cycloexpansion and Cycloreversion Products by Photolysis of Azetidinediones

Compd	Cycloexpansion (% of IX)	Cycloreversion (% of X and XI)	Quantum yield
I	80	20	0.65
II	80	20	0.65
III	80		
IV	60	40	0.41
V	80	20	0.44
VII	5 <sup>b</sup>	90 <sup>b</sup>	0.12
VIII	44 <sup>c</sup>	27 <sup>c</sup>	

<sup>a</sup> Determined by NMR analysis of reaction mixtures obtained by irradiation at 253.7 nm in methanol. <sup>b</sup> 5% decarbonylation is observed. <sup>c</sup> 29% of unidentified photodegradation products generated from 2-methoxy-3,5,5-triphenyl-4-oxazolidone (IX).

mains low, even when the presence of a 3-phenyl group as in V and VI lowers the IP appreciably.

For dione VIII the 1-phenyl and 3-phenyl substituents will lower the dissociation energy of both N-CO and C-CO in the molecular ion. Competition between intermediates a and b is expected to occur. The observation that the AP- (metastable ketene ion) for VIII (8.46 eV) lies 0.25 eV below the IP for VII (8.71 eV) is consistent with an important contribution of the pathway involving intermediate a. Indeed, the IP for VII can be regarded as the lower limit for the energy required to produce ion b from VII and also, to a first approximation, to produce ion b from VIII. The fact that the AP (metastable ketene ion) for VIII lies below this limit, in conjunction with the very low  $\epsilon_0$  observed, indicates that the reaction pathway involving primary fission of C-CO competes favorably with fission of N-CO.

**Relations between the Mass Spectral and Photochemical Reactions.** A striking analogy is found between the electron-impact induced and the photochemical reactions (Table IV) of the azetidinediones. For VII the low quantum yield for photocycloreversion correlates with the high abundance of the molecular ion and with the high activation energy for its cycloreversion. Both the electron impact induced and the photochemical reaction probably involves largely intermediates of type b. In spite of the different natures of diradical B and ion radical b the 1-phenyl group must exert similar stabilizing effects in both intermediates.

The mass spectral and photochemical results for VIII, which shares the 1-phenyl group with VII, indicate a considerably decreased stabilization for type b intermediates. Here both N-CO and C-CO are strongly activated; hence, the formation and decomposition of type a and b intermediates will be fast, competitive processes. The very low abundance of the molecular ion and the low activation energy for its decomposition are consistent with this interpretation. The high quantum yield for the other diones correlates with the small activation energy for decomposition of the molecular ion. Evidently photocycloexpansion must involve intermediate A, while the oxacarbene C produced by rearrangement of diradical A is stabilized by the addition of CH<sub>3</sub>OH.

The unimolecular nature of the mass spectral reaction prohibits trapping of the postulated analogous intermediates a and (possibly) c, but the increase of  $T$  and  $T/\epsilon_{\text{excess}}(m^*)$  in the series IV, I, and V correlates with a corresponding increase of the yield of photocycloexpansion products.

### Experimental Section

Mass spectra were recorded on an AEI MS902S instrument operating at 8 kV accelerating voltage, trap current 500  $\mu$ A, and 70 eV ionization energy. The 15 and 10 eV spectra were run with a trap current of 100  $\mu$ A. Samples were introduced into the ion source operated at 70° via a glass reservoir heated at 100–120° or via a direct inlet system. Precise mass measurements were per-

formed with the peak matching technique at a resolving power of 10,000.

Ionization efficiency curves were determined by using the heated inlet system and also by using a heated or cooled direct insertion probe. In the latter case the crystalline compounds, either pure or dissolved in ether, were heated gently in a glass capillary to effect evaporation of the ether and (or) fusion of the compound. This procedure resulted in a regular evaporation from the semicrystalline residue and a constant ion current. The ion source temperature was 70°. The repeller potential was set to zero and the trap current to 10  $\mu$ A. Benzene (electron-impact IP = 9.50 eV) was used as the calibrant. The curves were interpreted with the semilogarithmic plot method<sup>16</sup> and the difference in electron volts for the curves of azetidinediones and benzene was read at 0.1% of the ion current at 50 eV. The AP of the metastable ketene ions, generated in the first drift region and refocused at the appropriate ESA potential, were measured without changing the ion source conditions.

Metastable peak widths at half-height were determined from plots of ion current vs. accelerating voltage. The latter was varied manually in the 7.000 V region by using the decade box of the peak matching system after reducing the ESA potential, necessary to transmit metastable ions at 7.750 eV, with a factor 1.1. Narrow settings of the energy-resolving  $\beta$  slit were used; the main beam width at half-height was about 3 V at 7000 V accelerating voltage. A fraction  $m_2/m_1$  ( $m_1$  = mass molecular ion,  $m_2$  = mass ketene ion) of this width was subtracted from the metastable peak width at half-height.  $T$  was calculated from this corrected metastable peak width ( $\Delta V$ ) using the formula<sup>3</sup>

$$T = \frac{m_2 e V_1}{16 m_3} \left( \frac{\Delta V}{V_1} \right)^2$$

where  $m_2$  = mass of ketene ion,  $m_3$  = mass of neutral,  $V_1$  = value of accelerating voltage at which the center of the metastable peak is transmitted.

The metastable peak shapes and intensities were not affected by admitting air as collision gas (pressure until  $10^{-5}$  Torr) in the ESA region.

Materials were prepared and purified by methods described elsewhere: I–III,<sup>42</sup> III,<sup>1</sup> IV–V,<sup>43</sup> and VII and VIII.<sup>44</sup> Compound VI was prepared as follows. Dione V (200 mg) was dissolved in dry acetone (2 ml) and to the solution were added K<sub>2</sub>CO<sub>3</sub> (500 mg), molecular sieve (pore diameter 4 Å, 200 mg), and methyl iodide (0.5 ml). The reaction vessel (test tube with glass joint) was closed and the solution was stirred for 2 days at room temperature. Ether (5 ml) was added to the reaction mixture, and the solution was filtered and evaporated. The oily residue was purified by preparative TLC on precoated silica gel plates (layer thickness 0.25 mm, Merck F254) using the solvent system benzene–chloroform (2:1).

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## Electrolyte-Induced Phase Transitions in Micellar Systems. A Proton and Carbon-13 Nuclear Magnetic Resonance Relaxation and Photochemical Study<sup>1</sup>

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**Abstract:** The electrolyte-induced phase transition from spherical to rod-shaped aggregates in aqueous micellar solutions of dodecylammonium chloride (DAC) has been studied by means of proton and <sup>13</sup>C NMR and photochemical techniques. The shape of the proton NMR spectrum is changed drastically upon the addition of the electrolyte (broadening of the resonance lines and a drop in the intensity of the lines). The relative efficiencies of various anions in inducing the transition were found to follow the lyotropic series Cl<sup>-</sup> < Br<sup>-</sup> = NO<sub>3</sub><sup>-</sup> < ClO<sub>4</sub><sup>-</sup>. The relaxation times or T<sub>1</sub> values for different protons of the DAC molecule are not as greatly affected by the structural changes. The <sup>13</sup>C spectrum does not change significantly. T<sub>1</sub> values for backbone carbons (C<sub>2</sub> to C<sub>9</sub>) are reduced, that of the α carbon is increased, and those of C<sub>10</sub> to C<sub>12</sub> remain unaffected upon the formation of rod-shaped aggregate. The dynamics of pyrene monomer and excimer fluorescence in the two structural forms was investigated by 347.1 nm ruby laser photolysis. The pyrene excimer yield depends both on the distribution of pyrene among the micelles and their rate of diffusion. In rod-shaped aggregates the diffusion occurs along the longitudinal axis of the rod with a rate which is about 2.5 times smaller than in a spherical micelle. The permeability of the spherical and rod-shaped micelles with respect to various species was studied by a kinetic analysis of the quenching of pyrene monomer fluorescence. Differences in the quenching efficiencies observed for ionic quenchers reflect a decreased surface charge in the rod-like structures. Quenching experiments with Br<sup>-</sup> counterions yield an effective half-lifetime for the radial diffusion of the probe from the center to the periphery of the rods. Finally fluorescence depolarization studies using 2-methylanthracene and 1-anilino-8-naphthalenesulfonate as probes are reported. The former indicates a considerable increase in microviscosity of the micellar interior upon the formation of rods while the latter reveals no significant changes in the micellar surface region.

Micellar systems provide useful structural and functional models for more complex bioaggregates.<sup>2</sup> Possible analogies between micellar catalysis and enzyme catalysis have also been suggested.<sup>3</sup> Recently several interesting features of micellar assemblies have been established by the use of physicochemical techniques such as NMR<sup>4</sup> (chemical shift analysis as well as relaxation studies), ESR nitroxide<sup>5</sup> spin labeling, and fluorescent probe analysis.<sup>6</sup> While at relatively low concentrations surfactant molecules are associated in spherical micelles, other structural forms such as rods or bilayers occur in more concentrated solution.<sup>7</sup> A schematic illustration of such molecular organizations is presented in Figure 1. Similar structures can be produced, alternatively, by the addition of electrolytes.<sup>8</sup> Large micelles with a rod-like shape or bilayers are probably more suitable models for biomembranes. Hence a study of the formation and properties of these structures should provide some clues on the forces that govern the hydrophobic interactions in biological

systems and also would lead to a better understanding of complex processes exhibited by these systems such as polymorphisms (thermotropic and lyotropic) and micellar catalysis of organic reactions.

The present investigation is directed toward an analysis of the electrolyte-induced sphere-rod transitions in surfactant solutions. Typical systems where these type of transitions occur are summarized in Table I together with literature data on the micellar shape and aggregation numbers. Of these dodecylammonium chloride/sodium chloride [abbreviated hereafter as DAC/NaCl] was selected as a suitable model system for detailed study. Several techniques were employed to monitor changes in the dynamic and static properties of the micellar assemblies, associated with the transition.

In the first part of the paper <sup>1</sup>H and <sup>13</sup>C NMR results are presented to characterize the sphere-rod transition. While a line-shape analysis of the proton and carbon-13