either a radical pair formed *via* the excited state of phenoxide ion or one formed by diffusion together of two noninteracting radicals. Let us consider the former. Since photoelectron ejection appears to occur *via* the singlet rather than the triplet state,[17] eq 1 predicts absorption which is in contradiction with the emission observed experimentally. Therefore, a radical pair formed *via* the excited state of phenoxide ion cannot account for the experimental results. On the other hand, a radical pair formed by diffusion together of a phenoxyl radical and a hydrated electron can account for the results since eq 1 predicts emission for this pair. We have ruled out this possibility by comparing the intensity of the emission lines obtained for an air-saturated solution with the intensity of the emission lines obtained for a degassed sample at about 2 μ pressure. The concentration of oxygen in an air-saturated solution is about 10^{-4} *M*. Since the rate constant for reaction of oxygen with hydrated electron is[30] $1.88 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, the rate of reaction of the hydrated electron with oxygen should be competitive with the rate of reaction with the phenoxyl radical in the air-saturated solution. In the degassed sample, the concentration of oxygen is decreased by five orders of magnitude. Consequently, if the spin polarization occurs *via* Scheme III, the intensity of the emission lines observed in the air-saturated solution should differ from the intensity for the degassed solution. It was found that there is no significant difference. Thus, we conclude that Scheme III is not consistent with the experimental results. In addition, a dimerization of phenoxyl radicals cannot account for the polarization since Δg is zero for the radical pair in this case. When Δg is zero, no net polarization occurs.[22]

Finally, in Scheme I, the formation of the hydrated electron is suggested, but a mechanism for its disappearance has not been discussed. The epr and nmr results give us no information concerning the reaction of this species. Probably it disappears according to various mechanisms which do not alter the mechanism proposed in Scheme I. For example, the hydrated electron could combine with any of the observed radicals or react with water to form hydroxide ion and hydrogen.[31]

Acknowledgment. The authors are grateful to A. A. Lamola for helpful suggestions and to M. Fujimoto of the Physics Department for allowing the use of the Varian E12. This work has been supported in part by NRC Grant No. A5874, PRF Grant No. PR4904, and DRB Grant No. 953096.

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Hindered Rotation in Halogen and Pseudohalogen Carbon-Substituted Amides

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Abstract: The barrier to rotation about the amido C–N bond has been measured for five C-substituted *N,N*-dimethylamides. Dimethylcarbamyl chloride has been extensively studied previously, and a critical survey of the systematic errors in all determinations has been achieved by a composite plot of the derived parameters $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$. It is clear that, for the ten available results for this molecule, the linear relationship of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is an artifact of the experiment and that all results considered extrapolate at $\Delta S^{\ddagger} = 0$ to the same value of $\Delta G^{\ddagger}$. The complete line-shape-fit studies of the modified proton magnetic resonance spectra reported here take account of chemical shift dependence with temperature, the Lorentzian form of a line-shape standard whose inhomogeneously broadened resonance does not exceed 0.4 Hz, a defined error analysis over all data points of less than 2%, and a measurement of a uniform temperature to a maximum error of ±0.5°. The activation parameters are reported for the azide, cyanide, thiocyanate, and the bromide, and these are considered in terms of simple valence-bond structures. The chemical shift between methyl peaks in *N,N*-dimethylcarbamyl azide is only 1.8 Hz, and it has not been possible to assign the peaks at this stage. The azide group behaves somewhat like the fluorine substituent studied previously.

The application of nmr to the study of hindered internal rotation about partial double bonds has become very widespread, as outlined in recent comprehensive reviews.[1,2] In general, however, these parameters for any given compound show a large variance, and a semiquantitative correlation of the data available for a related series of compounds has not been possible. Although a number of substituted *N,N*-dimethylamides have been investigated using nmr, the only example of a rotational barrier that has been studied under the same experimental conditions in independent laboratories and for which all of the activation parameters are consistent within calculated error limits is that of *N,N*-dimethylformamide (DMF).[3,4] Thus the data presented in this paper for another well-

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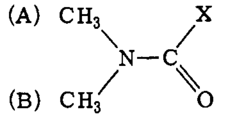
studied molecule, *N,N*-dimethylcarbamyl chloride (DMCC), are intended for comparison with that available from a recent independent complete line-shape study.[5]

Following a recent theoretical treatment of multisite chemical exchange effects on a nmr spectrum in the first-order limit,[6] a series of hindered rotation barriers in amido-type structures were measured.[7,8] In the general structure I, long-range *J* coupling from X to the *cis*- and *trans*-methyl group protons often complicates the line shape of the methyl groups interchanging between two simple chemically shifted sites.[7] For example, in *N,N*-dimethylcarbamyl fluoride (DMCF), with X = F, the chemical shift between methyl groups A and B varies from 2.2 to 1.4 Hz at 100 MHz over the interesting region where exchange modified the spectrum and long-range couplings of 0.3 ± 0.05 Hz (cis) and 0.8 ± 0.05 Hz (trans) are measured. Thus a full line-shape analysis, using multi-site exchange theory, is necessary in order to gain a quantitatively accurate estimate of the energy barrier for rotation about the N–C bond. When X = CF_3 or CH_3, the methyl signals are two quadruplets, and in the latter case resolution of these multiplets is beyond the capabilities of the spectrometer.[8] In these systems a complete line-shape fit involves all eight sites and the ambiguity of relative signs of the long-range coupling constants. In almost all previous studies the simple two-site exchange theory[9] has been used, and often approximate values of rates of hindered rotation have been obtained from other simple characteristics of the nmr line shapes such as line width, maximum to minimum intensity ratios, and moments of the line shape. It is now apparent that not only must a complete line-shape fit of the unsaturated steady-state spectrum[10] be accomplished, but all distinguishable sites having Larmor frequencies which are modulated by the chemical exchange process must be included.[7,8] Spin-echo studies of exchange in amides has also been restricted to a two-site analysis,[11,12] even though for X nuclei removed from the resonance condition, as in the case for X = CF_3,[13] there is an effective decoupling only under special experimental conditions.[14] Work in this laboratory, and in that of Gutowsky and coworkers, has shown that systematic errors persist in the Carr–Purcell method of studying chemical exchange.[3,13,15] The activation energies, obtained independently in these two laboratories, are associated with alarmingly large negative entropies of activation for simple hindered rotations.[10,16] We therefore conclude that for kinetic measurements leading to reliable thermodynamic parameters complete line-shape fitting, using multi-site theory and allowing for temperature dependences of the spin-site frequencies[6,7] where necessary, is required with an overall deviation between experimental and computed line shapes of less than 2%. This is further exemplified by a comparison of the data now available for DMCC.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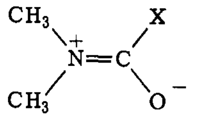
Ib

Earlier measurements[7,8] using multi-site theory for amide systems have now been extended in this paper to include the halo and pseudohalo substituents X = Cl, Br, CN, NCS, and N_3. The work of Rogers and Woodbrey[17] shows that the barrier to rotation in amides is strongly influenced by the substituent X. Activation energies were discussed qualitatively in terms of the effect of a given substituent upon the bond order of the N–C bond. Although a number of calculations based upon simple Hückel molecular orbital (HMO) theory have been reported for amides,[18–20] the only calculations of this type of related compounds are those given by Sandström[21] for a series of substituted *N,N*-dimethylthioamides. In the latter study, the $\Delta G^{\ddagger}$ obtained from nmr data shows only a crude correlation with N–C π-bond orders derived using a modified π-Hückel method, while a slightly improved correlation is obtained with the corresponding loss in π-electron energy which occurs when the dimethylamino group is rotated with respect to the thiocarbonyl group about the N–C bond. The correlations obtained here are discussed in terms of a simple valence-bond model for the hindered rotation process.

Experimental Section

(i) **Preparation of Compounds.** *N,N*-**Dimethylcarbamyl chloride** (DMCC) was obtained from K & K Laboratories Co. Ltd., and was purified by a double vacuum distillation and stored over molecular sieves. Experimental and literature physical constants agreed for this compound. As DMCC is a liquid (bp 165° at 760 mm), this amide was studied neat and in the nonpolar solvent carbon tetrachloride (6 mol %). In preparing the nmr samples, 2 mol % of tetramethylsilane (TMS) was added to provide a stable field-frequency lock signal, and 2 mol % of dioxane was also added as a line-shape standard. The nmr samples were thoroughly degassed by the usual freeze–pump–thaw cycles.

N,N-**Dimethylcarbamyl bromide** (DMCB) was prepared by saturating ~10 g of DMCC[22] by bubbling a mixture of HBr and N_2 gases through the neat liquid chloride kept at 0°. The N_2 stream removed any HCl or Cl_2 formed and significantly increased the yield of the carbamyl bromide. The bromide was purified by multiple distillations at ~10 mm, the boiling point of the final product being 63° at this pressure. The product was identified by nmr and was shown to contain ~2% of the carbamyl chloride, this being verified by the following elemental analysis.

	C	H	Br	Br + Cl
Calcd, %	23.68	3.95	52.63	
Found, %	24.54	4.30		54.11

This liquid amide was studied as the neat compound, the nmr sample being prepared as described for DMCC.

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N,N-**Dimethylcarbamyl cyanide** (DMCN) was obtained by a modified preparation originally reported by Atkinson.[23] A solution of 32 g of ethyl oxamate (Aldrich Chemical Co.) and 70 ml of benzene was prepared, and dimethylamine was bubbled through for 1 hr. The resulting mixture was warmed on a hot plate with a stirrer, while 40 g of phosphorus pentoxide was added slowly, so that the temperature did not rise appreciably. The mixture was heated at reflux, stirred for an additional hour, and then filtered hot, and the remaining residue was washed with hot benzene. Evaporation of the benzene yielded about 3 g of crude DMCN. The compound was purified by vacuum distillation (bp 176° (760 mm)) and characterized by comparison with previous nmr data on DMCN obtained by Sandström.[24] Nmr samples were prepared as 5.6 and 18 mol % solutions in *sym*-tetrachloroethane with 2 % hexamethyldisiloxane for a field-frequency lock signal.

N,N-**Dimethylcarbamyl isothiocyanate** (DMNCS) was prepared by a modification of the procedure of Spurlock, *et al.*[25] DMCC (25 g) and 150 ml of acetronitrile were stirred and heated at reflux, while 22.7 g of potassium thiocyanate was added in portions over a period of 1 hr. The refluxing and stirring was continued for an additional 2.5 hr; then the resulting slurry was cooled and filtered and the solvent was removed on a rotary evaporator. The residue was taken up in ether, washed with a small quantity of water (10–15 ml), and dried over molecular sieves, and the ether was evaporated. Distillation of the crude product gave about 7 g (less than 20 % yield) of pure DMNCS: bp 44–46° (0.4–0.6 mm), n^{25}D 1.5475. The infrared spectrum agreed with the pertinent data provided by Spurlock, *et al.* Because of the rapid dimerization of DMNCS, an nmr sample was made up immediately using *n*-octane as solvent, with 10 mol % DMNCS and about 2.5 mol % each of dioxane and TMS. Further samples were made up in *sym*-tetrachloroethane and carbon tetrachloride, but dimerization of the DMNCS occurred over a period of about 48 hr[25] and nmr studies with varied solvents were abandoned for this molecule.

N,N-**Dimethylcarbamyl azide** (DMCN$_3$) was prepared by two different methods; that described by Stolle[26] for the diphenyl compound gave extremely poor yields for the dimethylcarbamyl azide. The successful preparation was achieved by exchange in acetonitrile as solvent, between DMCC and sodium azide. DMCC (10 g) was added slowly (over 75 min) to an agitated refluxing slurry of sodium azide (7 g) in acetonitrile (50 ml). The reaction progress was followed by nmr spectra. After 24 hr the mixture was filtered and the acetonitrile was removed on a rotary evaporator. The resulting liquid was distilled at 62° and 15 ± 2 mm to yield over 90% of the colorless DMCN$_3$. The DMCN$_3$ is stable at room temperature and did not decompose at 80° in a sealed nmr tube. Jensen, *et al.*,[27] report this compound with a boiling point of 58° at 14–15 mm. The infrared spectrum has been compared with data published by Jensen, *et al.*, and Lieber, *et al.*,[28] who erroneously reported that the compound melts at 59°. The solution for nmr studies contained 85 mol % carbon tetrachloride, 10 mol % DMCN$_3$, 2.5 mol % dioxane, and 2.5 mol % TMS and was dried over 4A molecular sieves. The nmr sample was thoroughly degassed and sealed under nitrogen (to about 30 cm) in a thin-walled nmr tube of 5-mm o.d.

(ii) **Methods.** Studies of the nmr spectra of DMCC and DMCB were made using a JEOLCO JNM-C-60H spectrometer operating at 60 MHz in the internal field-frequency lock mode and equipped with a JES-VT-2 variable temperature controller for the sample. The temperature is normally monitored by a thermocouple placed near the sample in the temperature control gas stream. As a temperature measurement is critical in quantitative kinetic studies, especially when it is only possible to apply complete line-shape analyses over a relatively small temperature range, the temperature was calibrated with a second thermocouple immersed in the same volume of sample contained in an open nonspinning nmr tube and also by replacing the exchange sample with an ethylene glycol sample. In addition, the temperature was checked before and after a number of spectra were recorded. While the use of the nonspinning sample does not give a reliable measurement of the spinning sample temperature, the instrument thermocouple temperature reading can be accurately correlated with that given from the ethylene glycol chemical shift–temperature equation reported by Van Geet.[29] The absolute error in the sample temperature measurement was estimated to be ±0.3°, and the sample temperature was constant within these limits over the recording time for a number of spectra at a given controller temperature setting. Thus, in general, it is possible to use the instrument thermocouple measurements calibrated at four temperatures with the glycol sample to reduce the time involved with continual sample replacement. Sweep rates as low as 0.05 Hz sec^{-1} were used to ensure a good approximation to slow passage conditions, and spectra were checked for possible distortion due to saturation.[6] At each temperature, field curvature and homogeneity and rf phase adjustments were made to ensure reproduction of the true spectral line shape. The resultant line width at half-maximum of the reference peak was held within the range 0.3–0.5 Hz. Multiple spectra were obtained at each temperature, and any spectra that were not precisely reproducible were discarded.

Studies of DMCN, DMNCS, and DMCN$_3$ were made at 100 MHz in the field sweep mode of a Varian HA-100, locked to a TMS or hexamethyldisiloxane internal reference. The standard variable-temperature assembly provided by Varian with this equipment was used for observing spectra at other than ambient temperature. Measurements of sample temperature were made from either methanol OH or glycol OH chemical shifts,[29] and these temperatures are assigned a maximum error of ±0.5°. Precautions were taken to avoid signal saturation by varying the rf power levels over a wide range and observing signal amplitudes. Each sample contained a line-shape standard, preferably a nonpolar compound with a single resonance peak near the methyl peaks with exchange modified spectra that had no complications of chemical exchange over the range of interest. The homogeneity controls were adjusted for this line-shape standard so as to achieve a Lorentzian line shape with a half-width of 0.4 Hz or less (often 0.15 Hz).

Experimental data points were tabulated for at least 50 frequencies across the exchange modified spectrum, including enough points outside the proton resonance region to reliably define zero intensity. In the earlier studies of DMCC and DMCB the intensity measurements were obtained by visual reading of spectra on the appropriate calibrated chart paper. Calibrations were always checked for each spectrum by reading several marker points on the chart as a difference count (±0.1 Hz total error) of the lock and observation channels of the spectrometer. In later studies with DMCN, DMNCS, and DMCN$_3$ the spectral intensities were directly digitized by interfacing the HA-100 with a Fabritek FT-1070 4K multi-channel analyzer and reading the digital counts in one-quarter of the memory for at least 100 points in the spectrum. It was convenient to store four spectra using one-quarter of the memory for each recording, and all frequency calibrations were made automatically through marker pulses from the interface unit.

For each of the amides studied here, the A and B methyl groups form a simple equal population two-site exchange system, and the modified steady-state nmr absorption mode line shape is defined in terms of 2×2 rate and site frequency matrices.[6] Also, in this particular case, an analytical form for the line-shape equation can be derived.[6,30] A Fortran IV computer program GPLONK[6,7] has been developed for efficient iterlative line-shape fitting of digitized experimental data. This program uses a rapidly convergent search routine, with the option of varying both the rate constant for the exchange process and the site frequencies, to avoid the generally unreliable convergence associated with a standard nonlinear least-squares regression analysis for exchange modified line shapes. For DMCN, DMNCS, and DMCN$_3$, the temperature dependences of the site frequencies and the methyl chemical shift differences 2Ω[6] are especially significant in the line-shape fitting procedure. Having allowed for chemical shift temperature dependence, there are two possible sources of error in the complete line-shape fitting method that should be mentioned. Firstly, it is implicitly assumed that the nmr line shape is exactly Lorentzian in the absence of exchange effects.[6,30,31] It is well known, however, that the observed line shape is a convolution of the true line shape with the spectrometer shape function,[32,33] and this function is determined by the magnetic field

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Table I. Activation Parameters for Hindered Rotation about the Amido C–N Bond in the Molecules DMCC, DMCB, DMCCN, DMNCS, and $DMCN_3$[a]

Compound	Solvent concn	Temp range, °C	ΔE_a, kcal mol^{-1}	$\Delta H^{\ddagger}$ (25°), kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
DMCC	6% in CCl_4	+0.5–137.1	17.1 ± 0.5	16.5	−0.6 ± 1.5	16.5 ± 0.5
DMCC	Neat	+28.7–50.8	17.6 ± 0.5	17.1	+0.8 ± 1.6	16.8 ± 0.5
DMCB	Neat	−10.2–61.6	15.3 ± 0.4	14.7	−3.3 ± 1.2	15.7 ± 0.4
DMCCN	5.6% in $(CHCl_2)_2$	+98.8–164.0	22.1 ± 0.6	21.5	+0.5 ± 1.5	21.4 ± 0.6
DMCCN	18% in $(CHCl_2)_2$	+101.8–172.2	22.8 ± 0.3	22.2	+1.0 ± 0.6	21.9 ± 0.3
DMNCS	10% in *n*-octane	+39.6–107.4	18.8 ± 0.5	18.2	−0.9 ± 1.5	18.4 ± 0.5
$DMCN_3$	10% in CCl_4	+12.6–80.1	18.2 ± 0.5	17.6	−0.3 ± 1.4	17.7 ± 0.5

[a] In two cases variations of concentration and solvent were investigated.

homogeneity which is not necessarily Lorentzian within the sample volume. In principle it is possible to allow for non-Lorentzian character in the line-shape calculations, but this requires accurate digital data for the reference line which has a width of 0.5 Hz or less and also the numerical evaluation of a convolution integral for each spectral data point. A series of computer calculations on simulated line shapes, however, showed that this refinement is unnecessary unless the reference line shape shows significant visual deviation from Lorentzian form, such a deviation being most evident in the wings of the spectral line. Therefore, as already indicated, errors from this source are minimized by adjusting the spectrometer field homogeneity controls to obtain a reference line shape best approximating the symmetrical Lorentzian form. Secondly, there is an uncertainty in the value assigned to the transverse relaxation time T_2, and this introduces large errors in the rate constants determined in the very slow and very fast exchange limits,[10] which in turn are especially important for the accurate evaluation of an activation energy from data over as large a range of temperature as possible. Although values determined from the modified line shape in the limit of negligible exchange have been used,[34,35] we prefer to use a value derived from a reference line over the entire temperature range of interest. In all cases studied here, careful checks in the limit of negligible exchange showed that the methyl line widths were close to identical with the reference line width, indicating that there is no broadening due to nitrogen–methyl or methyl–methyl couplings.

The activation parameters are determined using standard techniques, as previously described.[7]

Results and Discussion

***N*,*N*-Dimethylcarbamyl Chloride.** Initially this substituted amide was studied as the neat liquid (except for the 2% TMS and dioxane line-shape standard), and typical line-shape fits for the equal population, two-site exchange system were obtained using the computer program GPLONK. The iterative line-shape fitting is based upon a search routine which rapidly converges to a "best fit" parameter value through a series of optimal parameter increments. The "best fit" value corresponds to a minimum in the sum of squares of deviations $S = \Sigma_{i=1}{}^N[V'(x_i) - V(x_i)]^2$ for N data points, where $V(x_i)$ is the theoretical-line-shape amplitude for the frequency $x = x_i$, the line-shape function being normalized to the experimental data $V'(x_i)$. The methyl group relative chemical shift $2\Omega^6$ corresponding to minimum S values was 6.8 ± 0.2 Hz (at 60 MHz) over the temperature range −10 to 65°, and hence may be considered to be temperature independent. The mean deviation, calculated as $(1/N)\{\Sigma_{i=1}{}^N[V'(x_i) - V(x_i)]/V(x_i)\}100$, for the spectra is less than 2% in all cases. The activation energy, E_a, for the hindered rotation is determined as 17.64 ± 0.52 kcal mol^{-1}. The activation parameters calculated at 25° are included in Table I and are in good agreement with those obtained by Neuman, *et al.*[5] (E_a = 16.9 ± 0.5 kcal mol^{-1}, $\Delta G^{\ddagger}$ = 16.8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −1.6 ± 2.0 cal deg^{-1} mol^{-1}). It has previously been noted[3,5,10] that as increasing care is taken in obtaining kinetic data using nmr methods, the values of E_a and A tend to increase while the free energy of activation, $\Delta G^{\ddagger}$, remains nearly constant. The data presented here exemplify these trends. For hindered rotations in *N*,*N*-dimethyl amides the entropy of activation is expected to be relatively small. As this entropy change in liquids is most probably associated with a difference in the solvation structures for the ground and transition states, it is predicted that there will be a very small increase in entropy on formation of the transition state, because the dipole moment for this state is normally smaller than that for the approximately planar ground state.[2] Within the error bounds calculated as the statistical 95% confidence limits, this is shown to be the case for DMCC studied as a neat liquid. In comparison, the entropy of activation derived from spin-echo data is ∼−11 cal deg^{-1} mol^{-1}, and the corresponding activation energy for DMCC (neat) is 14.0 ± 0.9 kcal mol^{-1}.[12] It it is to be noted, however, that under the assumption that $\Delta S^{\ddagger} = 0$ the activation energy may be calculated from the spin-echo data at the coalescence temperature[10] to be 17.5 kcal mol^{-1}. In addition, the free energy of activation is determined as $\Delta G^{\ddagger}$ = 16.6 kcal mol^{-1}; *cf.* 16.8 kcal mol^{-1} in Table I.

Solute–solvent interactions for the strongly polar DMCC molecule (μ = 4.08 D)[36] may be expected to influence the magnitude of the barrier to hindered rotation. Thus DMCC was also studied as a dilute (6 mol %) solution in the nonpolar solvent CCl_4 to minimize such interactions. The kinetic data obtained from total line-shape analyses give a constant chemical shift 2Ω = 7.1 Hz at 60 MHz. The activation energy is determined as 17.05 ± 0.47 kcal mol^{-1}. The rate constants describing hindered rotation at any temperature are significantly higher in the dilute CCl_4 solution as shown in particular by the values of 39.3 ± 0.2°. At this temperature the rate constant in CCl_4 is 13.54 sec^{-1} compared with 11.74 in the neat liquid. The activation energy, however, shows only a small concentration dependence which is comparable with the experimental errors involved. The entropy of activation is very small and formally negative: $\Delta S^{\ddagger}$ = −0.6 ± 1.5 cal deg^{-1} mol^{-1}. Although the hindered rotation for this particular amide is shown to be nearly independent of solute concentration, the form of the mag-

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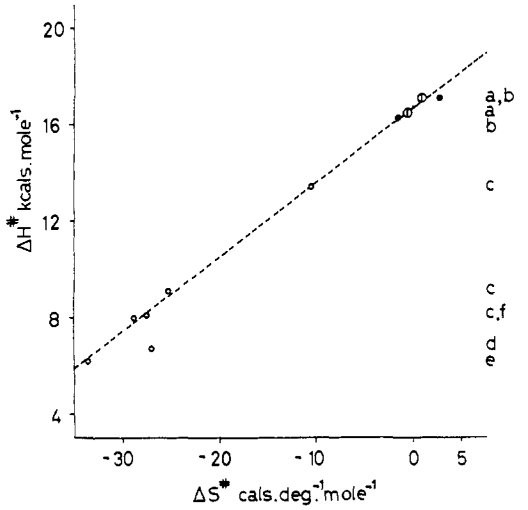


Figure 1. Variation of activation parameters $H^{\ddagger}$ and $S^{\ddagger}$ determined by nmr methods for hindered rotation in *N*,*N*-dimethylcarbamyl chloride. The lettered points correspond to the references listed below: (a) this work; (b) R. C. Neuman, D. N. Roark, and V. Jonas, *J. Amer. Chem. Soc.*, **89**, 3412 (1967); (c) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964); (d) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (e) J. C. Woodbrey and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 13 (1962); (f) E. Krakower, Ph.D. Thesis, University of British Columbia, 1967.

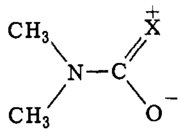
netic anisotropy of the carbonyl group,[37,38] which is assumed to be the dominant mechanism giving rise to the chemical shift between the *N*-methyl group cis and trans to this functional group, is changed significantly from that in the neat liquid system. The chemical shift difference is presumably due to a change in the form of specific solute–solvent interactions.

In order to consider the interrelationships between derived activation parameters, all data available for the hindered rotation in DMCC have been correlated. The $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values have been calculated for a fixed temperature of 25°. The overall variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as obtained using different methods of analysis and also different solvents and solute concentrations, is shown graphically in Figure 1. In general, systematic errors are shown to lead to higher E_a ($\Delta H^{\ddagger}$) values being associated with higher A ($\Delta S^{\ddagger}$) values, and *vice versa*. Except for a single data point in Figure 1, however, a linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is clearly shown, and this implies as suggested previously[1] that the free energy of activation, $\Delta G^{\ddagger}$, may be approximately invariant to systematic errors inherent in the determination of E_a and A. The mean of $\Delta G^{\ddagger}$ is 16.5 kcal mol^{-1} with an overall variation of only ± 0.3 kcal mol^{-1} for the published data referenced in the legend to Figure 1. This is to be compared with the value calculated from the linear correlation for $\Delta S^{\ddagger} = 0$, that is, $\Delta G^{\ddagger} = \Delta H^{\ddagger} = 16.6$ kcal mol^{-1}. The variation in ΔH for nearly identical chemical systems is of the order of 11 kcal mol^{-1}, included in the same set of data. Up to this point the only reliable parameter is $\Delta G^{\ddagger}$ for most studies of amides. While it is not possible to define the entropy of activation to better than ± 1.5 cal deg^{-1} mol^{-1}, values reported in this paper are generally zero to within experimental error.

There is a tendency for rate processes in solution to give enthalpy and entropy changes which compensate each other,[39,40] but in studies of amides such a result can be associated clearly with the systematic errors of measurement.

***N*,*N*-Dimethylcarbamyl Bromide.** This amide (DMCB) was studied as the neat liquid, as solute–solvent interactions were shown to have only a small effect on the hindered rotation in the similar DMCC system and upon the activation parameters. Line-shape fits could not be improved (within the rate constant error bounds) by introducing a temperature-dependent chemical shift 2Ω. The mean deviation for these fits is again less than 2%. Thus the cis–trans *N*-methyl chemical shift may be considered to be 5.4 ± 0.2 Hz at 60 MHz over the temperature range −15 to 70°. As this chemical shift is reduced by 20 and 32% from those for DMCC and the parent amide DMF (*N*,*N*-dimethylformamide, 2Ω = 8.1 Hz at 60 MHz[3]), respectively, considerable magnetic anisotropy associated with the C–Br bonding system is indicated. This anisotropy is of a form that partially compensates the shielding effect due to the C=O system in the region of the *N*-methyl groups, and this is also shown by the C–Cl bonding system in that the chemical shift 2Ω for DMCC is reduced by 16% from that for DMF. These chemical shift variations may arise in part from intermolecular interactions and electric field effects.[41]

The activation parameters calculated for DMCB at 25° are given in Table I, the energy of activation for the hindered rotation being $E_a = 15.25 \pm 0.36$ kcal mol^{-1}. Again the entropy of activation $\Delta S^{\ddagger} = -3.3 \pm 1.2$ cal deg^{-1} mol^{-1} is determined to be relatively small, as expected for the type of rate process under consideration. The free energy of activation is given as $\Delta G^{\ddagger} = 15.7 \pm 0.4$ kcal mol^{-1}, and is therefore lower than that for X = Cl (16.7), F (18.2), and H (21.0). This trend in $\Delta G^{\ddagger}$ values indicates that as the electronegativity of the substituent decreases, the barrier to hindered rotation also decreases. This is consistent with an increased contribution from the resonance structure II[17]



II

due to declocalization of formal lone-pair π electrons on the halogen atoms X, giving a lowered barrier to rotation about the N–C bond.

***N*,*N*-Dimethylcarbamyl Cyanide.** DMCN was studied as a dilute solution in the high boiling point solvent *sym*-tetrachloroethane $(CHCl_2)_2$, as line broadening due to chemical exchange of the *N*-methyl groups was measurable only above 90°. In this case, however, there is a significant temperature dependence of the chemical shift 2Ω and also of the chemical shifts ω_A and ω_B[6] for the methyl groups measured relative to internal hexamethyldisiloxane. For example, in the 5.6 mol % solution 2Ω varies between 25.0 and 26.6

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[37] P. T. Narisimhan and M. T. Rogers, *J. Phys. Chem.*, 63, 1388 (1959).

[38] L. Saunders and W. B. Whalley, *Tetrahedron*, 26, 119 (1970).

[39] K. H. Laidler, *Trans. Faraday Soc.*, 55, 1725 (1959).

[40] (a) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, 19, 1139 (1951); (b) J. E. Leffler, *J. Org. Chem.*, 20, 1202 (1955).

[41] W. T. Raynes and T. A. Sutherley, *Mol. Phys.*, 18, 129 (1970).

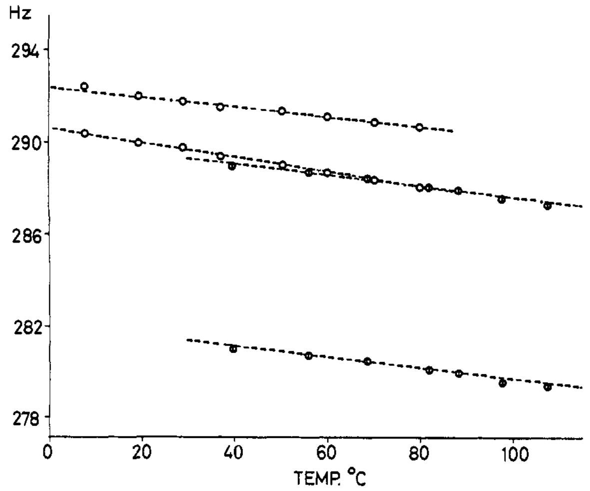
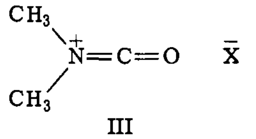


Figure 2. Temperature dependence of methyl group chemical shifts (relative to internal TMS at 100 MHz) for *N*,*N*-dimethylcarbamyl isothiocyanate (⦶) and *N*,*N*-dimethylcarbamyl azide (O).

Hz over the temperature range 98.8–164.0°, while ω_B changes by 2.8 Hz at 100 MHz.

As for DMCC, although the specific rate constants k at any temperature are significantly higher for the 5.6% $(CHCl_2)_2$ solution, the activation energies derived from the Arrhenius plots are 22.1 ± 0.6 and 22.8 ± 0.3 kcal mol^{-1} for the 5.6 and 18% solutions, respectively. Thus the activation parameters are essentially concentration independent. The negligible concentration dependence of E_a for the highly polar DMCN in the solvent $(CHCl_2)_2$ (μ = 1.4 D[42]) implies that the solute–solvent interactions are nonspecific and hence approximately independent of low solute concentrations. The $\Delta G^{\ddagger}$ value for DMCN is much higher than those for the halo-substituted *N*,*N*-dimethyl amides, and this is presumably due to the high electronegativity of the cyano group which not only decreases the contribution from the general resonance structure designated as II above but also increases the possible contribution from a resonance structure represented as



III

which enhances the barrier to rotation about the N–C bond, acting in conjunction with structure Ib.

***N*,*N*-Dimethylcarbamyl Isothiocyanate.** DMNCS was studied as a 10 mol % solution using the nonpolar solvent *n*-octane. Solute–solute interactions were minimized in this particular solvent as dimerization was not observable over a period of at least 72 hr, whereas such dimerization occurred readily in both CCl_4 and $(CHCl_2)_2$ solutions. The chemical shift 2Ω is 8.0 ± 0.2 Hz at 100 MHz and is constant within these limits over the temperature range 20–108°. The individual chemical shifts, ω_A and ω_B, show a consistent but relatively small temperature dependence as illustrated in Figure 2, varying by 1.6 Hz for a mean chemical shift of 280.4 Hz measured with respect to internal TMS over the same temperature range. Figure 2 illustrates the precision and consistency in measurements of chemical shifts by the line-shape method. The line-shape fits have minimum error over a range of $\omega_A - \omega_B$ of less than 0.1 Hz. The diamagnetic anisotropy of the C–NCS group acts to compensate the shielding effect due to the anisotropic C=O group in a manner analogous to the halogen C substituents, the effect being comparable with that for X = Br. The activation energy derived from the Arrhenius plot is E_a = 18.8 ± 0.5 kcal mol^{-1}, and the corresponding free energy of activation is $\Delta G^{\ddagger}$ = 18.4 ± 0.5 kcal mol^{-1}. Thus the barrier to rotation in DMNCS is relatively high, being very nearly the same as that for DMCF (X = F) but considerably lower than that for DMCN or DMF (X = H).[3] This indicates that the interaction of the isothiocyanate group with the carbonyl group is greater than that for the highly electronegative cyanide group.

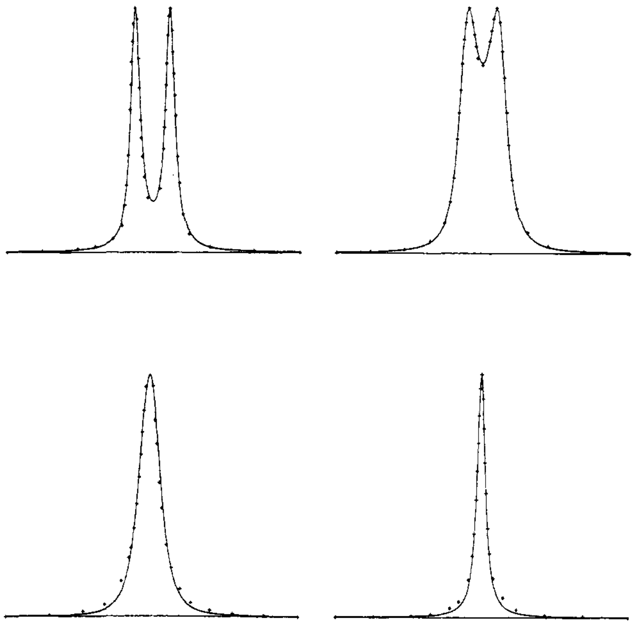


Figure 3. Line-shape fits for hindered rotation in *N*,*N*-dimethylcarbamyl azide. The frequency range for the computer plots is of the order of 12 Hz; *cf.* 2Ω = 1.95 Hz at 19.2°. The points are experimental data and the continuous line is the computed optimum fit.

***N*,*N*-Dimethylcarbamyl Azide.** $DMCN_3$ was studied as a 10 mol % solution in the nonpolar solvent CCl_4 over the temperature range 5–80°. The kinetic data were derived from the complete line-shape fits such as those illustrated in Figure 3. These line-shape fits are typical of all data obtained in this work. By using digitized spectral data and by systematic variation of the *N*-methyl chemical shifts, all mean deviations (as defined above) for the line-shape fits were of the order of 1.5%. Such precision again exemplifies the advantages of complete line-shape fitting, as the mean chemical shift 2Ω is only 1.8 Hz at 100 MHz, and reliable kinetic data have been obtained over a temperature interval of 68°. This relatively small cis–trans methyl chemical shift is approximately the same as that for DMCF[7] in the same solvent and at the same concentration. Thus the diamagnetic anisotropy associated with the azide group cancels the shielding effect due to the carbonyl group. In the case of DMCF it is possible to assign the A and B methyl resonances owing to the presence of long-range J couplings. As this assign-

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[42] *Beilstein*, 4th ed, 3rd suppl., 1, 161 (1958).

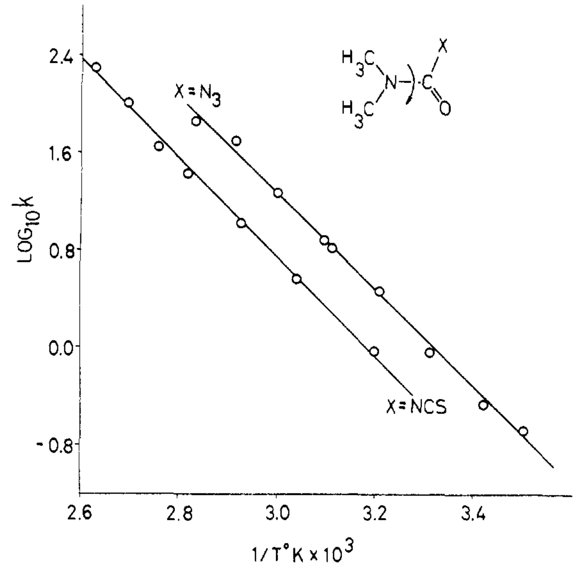
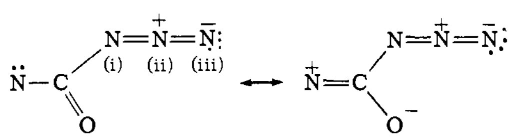


Figure 4. Arrhenius plots for *N*,*N*-dimethylcarbamyl isothiocyanate (X = NCS) and *N*,*N*-dimethylcarbamyl azide (X = N_3).

ment cannot be made for $DMCN_3$, the anisotropy of the azide group may be such that the normal assignment[3,7] is reversed. That is, geometrical factors aside, the principal components of the tensor describing the anisotropy for X = N_3 are comparable in magnitude with those for the C=O tensor. In turn, the long-range shielding of the complicated π-bonding azide group is comparable with or even more pronounced than the well-known shielding due to the C=O group. The Arrhenius plot for $DMCN_3$ is included with that for DMNCS in Figure 4 as representative of all amides studied here. The activation energy is given as E_a = 18.2 ± 0.5 kcal mol^{-1} with $\Delta S^{\ddagger} = -0.3 \pm 1.4$ cal deg^{-1} mol^{-1}. The free energy of activation is $\Delta G^{\ddagger} = 17.7 \pm 0.5$ kcal mol^{-1} which is significantly lower than that for DMNCS. This indicates that the interaction of the azide group with the carbonyl group in an amide structure is stronger than for the isothiocyanate group.

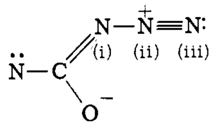
The interactions of the multiatomic substituents N_3, NCS, and CN with the amido group may now be considered in terms of a simple valence-bond[43] model. The molecular plane is taken to be the Cartesian *xy* plane so that p_z atomic orbitals are the normal π-type orbitals.

The basic structure for $DMCN_3$ may be represented as



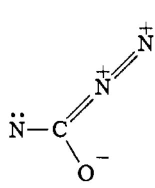
IVa IVb

in which the azide N atoms are sp^2, sp, and sp^2 hybridized, as numbered respectively. In IVa a π bond exists between N atoms i and ii, similar to that for the carbonyl group, and a π_y bond is formed between N atoms ii and iii for the formal charges as indicated. Also, the terminal N atom (iii) has two sets of lone-pair electrons in sp^2 σ orbitals located in the *xz* plane. Therefore, due to the overlap between these sp^2 orbitals and the N (ii) $2p_z$ atomic orbital, another resonance structure is readily formed through cross-conjugation with the carbonyl group.

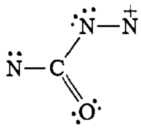


V

In this structure, the hybridization of N atoms i and ii is unchanged while the terminal N becomes sp hybridized with a single set of lone-pair electrons, and an additional π_z bond is formed between N atoms ii and iii. In this way the $-^{+}N{\equiv}N$ group becomes isoelectronic with the cyano group $-C{\equiv}N$. Two further resonance structures (VI and VII) are also possible in which the



VI

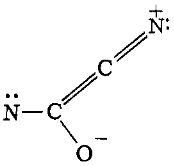


VII

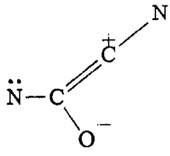
azide N atoms of VI are sp, sp, and sp^2 hybridized. As compared with structure IVa, this form corresponds to a change in hybridization for the N atom (i) and a formal rotation of the N(ii)–N(iii) group so that the lone-pair sp^2 hybrid orbitals are now located in the *xy* plane and π bonds from the terminal N atom are π_z, π_y, and π_z types. VII has azide atoms sp^3, sp, and sp with bonding similar to V except N(i) is rotated to prevent overlap with the carbon $2p_z$ orbital. For the first two of these resonance structures, cross-conjugation between the azide and carbonyl groups is enhanced, and hence the relative contribution of IVb is decreased and the barrier to rotation about the amide N–C bond is significantly lowered with respect to that for DMF (X = H), as is observed experimentally; *cf.* Table I.

Similar resonance structures may be considered for the isothiocyanate group which is isoelectronic (in valence electrons) with the azide group. In this case, however, the overlap between S lone pair sp^2 hybrid orbitals and the NCS C $2p_z$ atomic orbital[44] is considerably reduced, and hence the contribution from a structure analogous to V is also reduced. Thus the barrier to rotation in DMNCS is predicted to be higher than that for $DMCN_3$, which is indeed the case.

The cyanide group is distinctive from the NCS and N_3 substituents in that although resonance structures VIIIa and VIIIb are possible the associated electronic



VIIIa



VIIIb

energies are well above those of the major contributing structures designated generally as Ia and Ib in a prece-

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[43] G. W. Wheland "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 88.

[44] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

ding section. In VIII the cyano C atom is sp hybridized and a π_z bond is formed between C atoms, but the N^+ and C^+ (isoelectronic with B) atoms have vacant $2p_z$ orbitals in VIIIa and VIIIb, respectively. Therefore cross-conjugation between the cyanide and carbonyl groups is particularly unfavorable, and hence the barrier to rotation about the amide N–C bond is predicted to be comparable with that for DMF. As the species :C≡N: is stable, the limit resonance structure represented as III above may also be considered to contribute to the resonance hybrid for DMCN leading to an increased barrier to rotation. Thus it is seen that a simple valence-bond model is compatible with the observed $\Delta G^{\ddagger}$ value of 21.6 kcal mol^{-1}, being equal to or higher than that for DMF ($\Delta G^{\ddagger}$ = 21.0 kcal mol^{-1}).

The halogen substituents X = F, Cl, and Br may also be considered in the resonance form II if it is assumed that these atoms are sp^2 hybridized with formal lone pair electrons in a $2p_z$, $3p_z$, or $4p_z$ atomic orbital, respectively. The degree of cross-conjugation (and hence the contribution from resonance structure II) is then determined by the overlap between these p_z orbitals and a C $2p_z$ orbital and the respective halogen orbital electronegativities.[42] Thus the barrier to rotation is predicted to decrease in the order F > Cl > Br, again as is observed experimentally. Detailed semiempirical SCF–LCAO–MO calculations in the CNDO/2 and INDO approximations, which include orbital overlap and two-electron interactions, will be reported elsewhere in an effort to develop a more sophisticated model for the C-substituted amide bonding systems initially studied here.

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Long-Lived States of Rare Gas Ions. An Ion Kinetic Energy Study

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Abstract: Collision-induced ionization of rare gas ions ($m^+ + N \rightarrow m^{2+} + N + e^-$) has been studied by ion kinetic energy spectroscopy. Kinetic energy loss spectra, taken using 8-keV reactant ions, provide direct information on the internal energies of the rare gas ions. Typically, reaction occurs from three energy states or groups of states. These are the ground state, a state with energy very close to the second ionization potential, and an intermediate state. The onset of each peak in the energy loss spectrum corresponds to adiabatic ionization, and this allowed fairly accurate determinations (±1 eV) of the energies of the reactant ionic states. A state of Ne^+ (energy 27.7 eV above the ground state) was observed, apparently for the first time, to be long-lived ($\geqslant 10^{-5}$ sec). Experiments in which the ion accelerating voltage, collision gas pressure, and ionizing electron energy were varied confirmed the suggested major processes and provided further detail. For example, the highest energy state of the singly charged ions (probably due to high Rydberg levels) reacted both by a collision process and also by a unimolecular mechanism, the latter probably being pseudo-unimolecular and involving collisions with slit surfaces. Fine structure was sometimes observed in the kinetic energy loss spectra. In addition to the dominant 10/20 reaction, the 10/21 process was also observed.

The technique of ion kinetic energy spectroscopy (IKES)[2,3] has been applied to a wide range of problems in gaseous ion chemistry,[3] including studies on the structures and unimolecular reactions of ions, collision-induced reactions, the identification of isomeric compounds, and the determination of isotopic incorporation. The technique has proved particularly valuable in the study of multiply charged ions. Measurement of the kinetic energy (T) released in the fragmentations of doubly charged ions has been a key factor in allowing the proposal of structures for complex doubly charged ions, for studying isomerization in doubly charged ions, and in energetic studies on charge separation in simple doubly charged ions.[4]

Doubly charged ions formed in the ion chamber of a double-focusing mass spectrometer can undergo collision-induced charge exchange in the first field-free region of the instrument according to the general equation

$$m^{2+} + N \longrightarrow m^+ + N^+ \qquad (1)$$

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[1] On leave from Faculty of Technology and Metallurgy, University of Belgrade, Yugoslavia. This work was submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Science, Purdue University.

[2] (a) J. H. Beynon, J. W. Amy, and W. E. Baitinger, *Chem. Commun.*, 723 (1968); (b) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, 3, 313 (1969); (c) J. H. Beynon, W. E. Baitinger, and J. W. Amy, *ibid.*, 3, 55 (1969).

[3] For general reviews, see (a) J. H. Beynon, *Anal. Chem.*, 42, 97A (1970); (b) J. H. Beynon and R. G. Cooks, *Res./Develop.*, 22 (11), 26 (1971).

[4] (a) R. M. Caprioli, T. Ast, and J. H. Beynon, *Org. Mass Spectrom.*, 5, 417 (1971); (b) J. H. Beynon, R. M. Caprioli, and J. W. Richardson, *J. Amer. Chem. Soc.*, 93, 1852 (1971); (c) T. Ast and J. H. Beynon, paper presented at 19th Annual Conference on Mass Spectrometry and Allied Topics, ASMS, Atlanta, Ga., May, 1971.