# Gas-phase Thermolyses. Part 5.[1] Thermally-induced Rearrangement of Methyl Acetate in the Gas Phase

By **Lars Carlsen,* Helge Egsgaard,** and **Palle Pagsberg,** Chemistry Department, Risø National Laboratory, DK 4000 Roskilde, Denmark

The pure unimolecular gas-phase thermolysis of $^{18}O$-labelled methyl acetate has been investigated by the flash vacuum thermolysis–field-ionization mass spectrometry method, in combination with collision-activation mass spectrometry in the temperature range 1 043—1 404 K. Minor amounts of keten, as a result of 1,2-elimination of methanol, were detected. The predominant reaction is shown to be the intramolecular oxygen to oxygen methyl group migration. The isomerization is discussed in terms of vibrational excitation of specific in-plane bending modes observed for the methyl acetate molecule. The low-pressure rate constants for the isomerization at 1 253 and 1 404 K were calculated from the collision activation mass spectra.

THE gas-phase thermolyses of carboxylic acid esters, as well as the corresponding monothio-derivatives, have been investigated intensively during the past decade.[2-4] It has been demonstrated that thionocarboxylates, in the gas phase, can rearrange thermally into the thermodynamically more stable thiolo-esters. The energy of activation for the thiono–thiolo rearrangement has been estimated to be *ca.* 45 kcal mol$^{-1}$, slightly dependent of the nature of the ester alkyl group.[3,4] The reverse reaction has, however, to our knowledge not been observed, apparently owing to the thermodynamic stabilization of the thiolo-esters by *ca.* 20 kcal mol$^{-1}$ relative to the thiono-compounds.[4] On a possible thermally induced oxygen to oxygen alkyl group migration in carboxylic acid esters little information has appeared.[5] In 1971 Smith and his co-workers reported on the partial (40%) gas-phase thermolysis of $^{18}O$-labelled ethyl acetate. The reaction was carried out at 619 K in a stainless steel reactor at a pressure of *ca.* 500 Torr.[5,6] The mass spectrometric analysis of the reaction products revealed that only minor amounts of oxygen scrambling in the unreacted ester had occurred; the authors therefore excluded the intermediacy of an ion pair, in rapid equilibrium with the ester, as being responsible for the decomposition products, acetic acid and ethylene, formed upon thermolysis of ethyl acetate. No discussion of the observed oxygen scrambling was given. However, it should be noted that the thermolysis was carried out under relatively high pressure conditions, suggesting the possibility of important bimolecular reactions. Potential ester formation from acetic acid and ethylene [7] should be mentioned particularly.

In the present paper we report on the pure unimolecular gas-phase thermolysis of $^{18}O$-labelled methyl acetate (95% labelling in the carbonyl group) in the temperature range 1 043—1 404 K, focusing on possible $^{16}O$–$^{18}O$ methyl group migration.

## EXPERIMENTAL

*Methyl* [$^{18}O$]*Acetate.*—The $^{18}O$-labelled methyl acetate was prepared by hydrolysing 1-methoxyethylideneamine hydrochloride (1.09 g) [8] in pyridine (2 ml) by $H_2{}^{18}O$ (0.2 ml; Prochem; 99.5% enriched). After 18 h the precipitate ($NH_4Cl$ and unchanged imino ether hydrochloride) was removed by centrifugation. The supernatant liquid was poured into dilute hydrochloric acid and methyl acetate (*ca.* 0.5 ml) was stripped off by passing helium through the solution and collecting the ester in a liquid nitrogen trap. The purity was >99% by g.l.c. Minor amounts of water were detected in the sample.

*Flash Vacuum Thermolysis.*—The thermolyses were carried out using the flash vacuum thermolysis–field-ionization mass spectrometry (f.v.t.–f.i.m.s.) technique, which has been described in detail previously.[9] The method is based on a direct combination of a thermolysis unit, fulfilling the requirements for a Knudsen reactor, with a Varian MAT CH5D double-focusing mass spectrometer equipped with a combined electron impact ionization–field ionization–field desorption (e.i.–f.i.–f.d.) ion source. Collision activation (c.a.) mass spectra [10] were obtained by introducing helium as the collision gas *via* a needle valve into the second field free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The c.a. mass spectra of the single ions were obtained by scanning the electrostatic field.

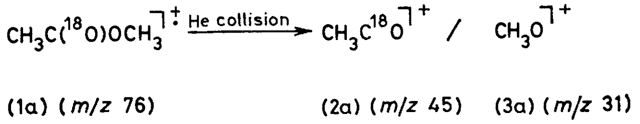
C.a. analyses of thermolysate mixtures are generally carried out on the single field ionized molecules.[9] However, the compound exhibiting the highest molecular weight in the reaction mixture, *i.e.* in the present case of undecomposed methyl [$^{18}O$]acetate (*M* 76), may advantageously be analysed by c.a. mass spectrometry of the molecular ion, if present, in the e.i. induced mass spectrum, as this ion evidently is not a result of e.i. induced fragmentation. The sensitivity of the c.a. analysis is thus considerably enhanced.

The f.i.–e.i. mass spectra following thermolyses were recorded with a scan rate of 50—100 a.u. s$^{-1}$. The e.i.–c.a. mass spectra of the single ions are recorded within 5 s (signal to noise ratio >1 000).

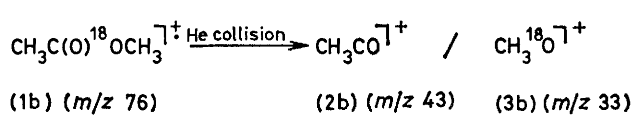
## RESULTS

We find that even at very high temperatures methyl acetate is rather stable and only decomposes to a minor extend. The products were keten and methanol, in agreement with the findings of Hurd and Blunck.[11] The field-ionization mass spectra of unthermolysed methyl [$^{18}O$]-acetate together with that obtained following thermolysis at 1 404 K are depicted in Figure 1.

In Figure 2a the e.i.–c.a. mass spectrum of the molecular ion of unthermolysed $CH_3C(^{18}O)OCH_3$ (1a) is shown.[12] No electron impact induced $^{16}O$–$^{18}O$ scrambling was observed (Scheme 1). In Figures 2b—d the c.a. mass spectra of the



SCHEME 1



SCHEME 2

molecular ions of undecomposed ester following thermolysis at 1 043, 1 253, and 1 404 K, respectively, are shown. The presence of the rearranged methyl acetate (1b) is unambiguously demonstrated by the appearance of the corresponding

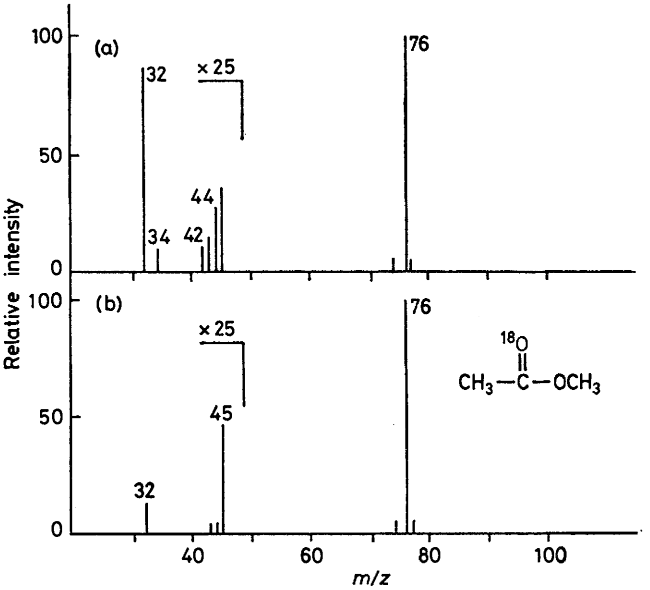


FIGURE 1 Field-ionization mass spectra of methyl [$^{18}O$]acetate (1a) following thermolysis at 1 404 K (a) and without thermolysis (b)

characteristic fragments (2b) and (3b) upon helium-collision (Scheme 2).

Based on Figure 2c and d the ratio (1b) : (1a) was calculated to be 0.09 and 0.31 following thermolysis at 1 253 and 1 404 K, respectively.

## DISCUSSION

The responsibility for the appearance of the rearranged ester (1b) can *a priori* be ascribed to two fundamentally different mechanisms, (a) a purely intramolecular methyl group migration *via* an electron-delocalized four-membered cyclic transition state or (b) a primary cleavage of the methyl–oxygen bond, followed by recombination to ester. The latter reaction can involve either a homolytic cleavage into the acetoxyl and methyl radicals or heterolytic formation of an ion pair. However, ion pair formation is much more energy demanding than homolytic radical generation and can accordingly be left out of consideration. On the other hand, it is necessary to discuss briefly the possible involvement of the acetoxyl–methyl radical pair.

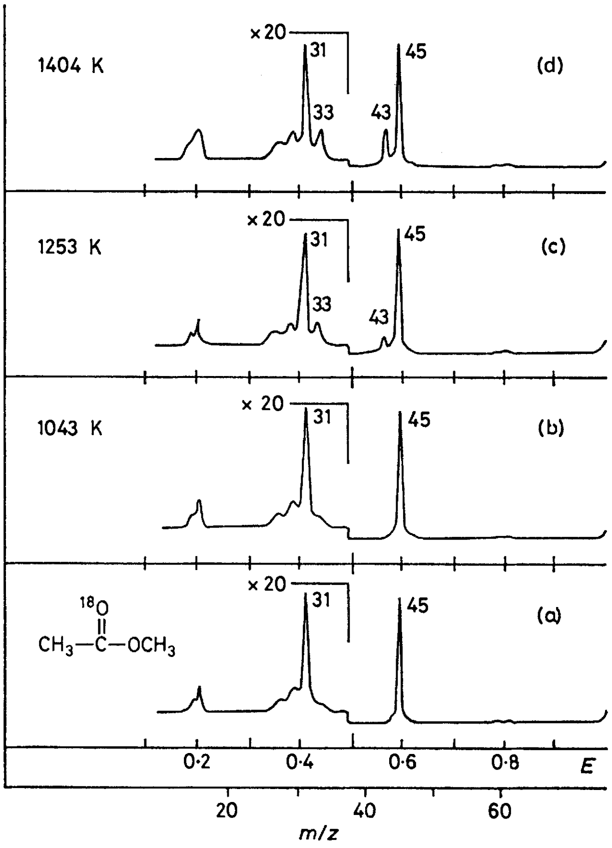


FIGURE 2 Collision activation mass spectra of the electron impact induced molecular ion of methyl [$^{18}O$]acetate (1a) without thermolysis (a) and following thermolysis at 1 043 K (b), 1 253 K (c), and 1 404 K (d), respectively

It has been reported that acetoxyl radicals decompose unimolecularly into methyl radicals and carbon dioxide. The rate constant ($k_1$) has been estimated to be of the order of $10^9$—$10^{10}$ $s^{-1}$.[13] The concurrent bimolecular radical reactions (*i.e.* acetoxyl–methyl or acetoxyl–acetoxyl, both leading to the formation of methyl acetate) proceed with rate constants $k_2$ *ca.* $10^{10}$ l $mol^{-1}$ $s^{-1}$,* which give rise to the kinetic expressions (1) and (2) for the disappearance of the acetoxyl radicals.

$$(\mathrm{d}[\mathrm{CH_3COO^\bullet}]/\mathrm{d}t)_1 = k_1[\mathrm{CH_3COO^\bullet}] \tag{1}$$

$$(\mathrm{d}[\mathrm{CH_3COO^\bullet}]/\mathrm{d}t)_2 = k_2[\mathrm{CH_3COO^\bullet}][\mathrm{R^\bullet}] \tag{2}$$

$$\mathrm{R^\bullet} = \mathrm{CH_3^\bullet} \text{ or } \mathrm{CH_3COO^\bullet}$$

Based on our previous study[9] the maximum radical concentrations in the reactor are estimated to be *ca.* $10^{-7}$ mol $l^{-1}$. On this background we conclude that under

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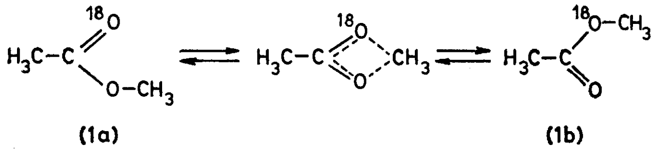
* Radical recombination reactions generally proceed with rate constants of *ca.* $10^8$—$10^{10}$ l $mol^{-1}$ $s^{-1}$, *i.e.* the choice of $k_2 = 10^{10}$ l $mol^{-1}$ $s^{-1}$ reflects the more conservative case.

the present conditions the unimolecular disappearance of possibly generated acetoxyl radicals will proceed at least $10^6$—$10^7$ times faster than the recombination reactions.

An experimental verification of our exclusion of the possible involvement of acetoxyl radicals in the apparent rearrangement (1a) ⟶ (1b) was obtained by co-thermolysis of the ester (1a) and [$^2H_3$]methyl acetate (*M* 77) (1c). In Figure 3 the e.i. mass spectrum of the mixture (1a)–(1c) is depicted together with the e.i. mass spectrum obtained following thermolysis of the mixture at 1 404 K. It is thus demonstrated that no methyl group crossover, which would give rise to simultaneous appearance of signals at *m*/*z* 74 and 79, takes place. The change in the mutual 43 : 45 ratio, due to thermolysis, is a reflection of methyl group migration only (*cf.* Figure 2). Consequently, we conclude that the methyl acetate isomerization proceeds purely intramolecularly *via* an electron-delocalized transition state (Scheme 3).



SCHEME 3

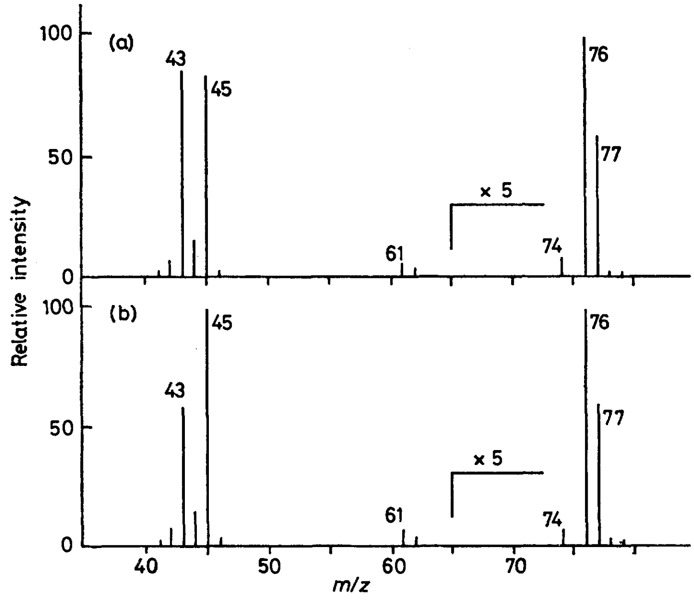


FIGURE 3 Electron impact mass spectra of a mixture of [$^{18}O$]-methyl acetate (1a) and [$^2H_3$]methyl acetate (1c) following thermolysis at 1 404 K (a) and without thermolysis (b)

On the basis of a vibrational assignment for methyl acetate, which demonstrates that the i.r. band contours are consistent with the ester possessing the *E*-configuration,[14,15] we suggest that the thermally induced isomerization of methyl acetate most probably proceeds through a vibrational excitation of two specific normal modes, which bring about the methyl group transfer.

It seems obvious that the vibrational modes, which are active in the methyl group transfer are the two in-plane bending modes $\nu_{15}$ 639 (OCO bend) and $\nu_{17}$ 303 cm$^{-1}$ (COC bend). Fairly strong coupling between these modes is demonstrated by the appearance of the corresponding combination mode 942 ($A'$) = 303 + 639 cm$^{-1}$ in the i.r. spectrum.[15] Since the reaction, as concluded above, proceeds through a four-centre transition state which, neglecting the isotopic effect on the oxygen–methyl bond length, of necessity is symmetric, the reaction co-ordinate may be expressed in terms of the combination of higher lying vibrational levels ($n\nu_{15} + m\nu_{17}$).

The threshold energy for the methyl group transfer can accordingly be expressed in terms of a critical set of quantum numbers ($n_c$, $m_c$) above which the two individual in-plane bending modes degenerate into one single ' hand-to-hand ' vibration (Figure 4).

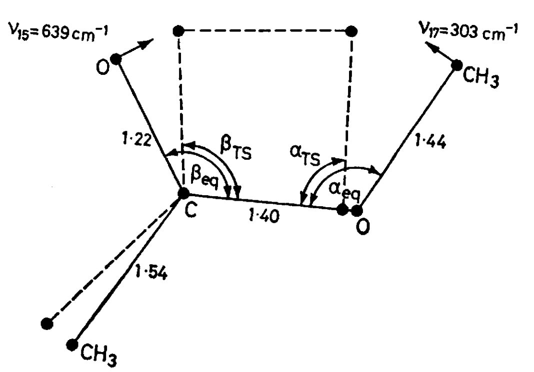


FIGURE 4 Structure of methyl acetate (——) and the transition state for the thermally induced isomerization (— — —)

A direct estimation of the energy of activation on this basis is, unfortunately, not possible, due to the lack of knowledge of the actual shapes of the two bending potentials involved. However, the rate constants for the (1a) ⟶ (1b) conversion can be calculated from the c.a. mass spectra depicted in Figures 2c and d.

The reaction can obviously be regarded as an equilibrium system (1a) $\rightleftarrows$ (1b) with concentrations [(1a)] = $[(1a)]_0$ and [(1b)] = 0 when the ester (1a) enters the reactor (*t* 0). Bearing in mind that the reactor fulfils the requirements for a Knudsen reactor,[9] we introduce the specific fluxes, $R_a$ and $R_b$, of the esters (1a) and (1b) into the reactor.[16] At low temperatures, *i.e.* no thermolysis taking place, $R_a = k_{ea}[(1a)]_0$ and $R_b = 0$, $k_{ea}$ being the unimolecular reactor escape rate constant[16] for the ester (1a). At elevated temperatures, where ester isomerization proceeds, the concentration of (1a) is smaller than $[(1a)]_0$, owing to the reaction taking place, and (1b) is generated, which affords expressions (3) and (4) for the stationary concentrations [(1a)] and [(1b)] in the reactor. $k_{eb}$ is the unimolecular escape rate constant of the ester (1b) and $k_1$ and $k_2$ refer to the (1a) ⟶ (1b) and (1b) ⟶ (1a) reactions, respectively. Elimination

$$R_a = k_{ea}[(1a)]_0 = k_{ea}[(1a)] + k_1[(1a)] - k_2[(1b)] \quad (3)$$

$$R_b = 0 \qquad = k_{eb}[(1b)] + k_2[(1b)] - k_1[(1a)] \quad (4)$$

of [(1b)] by equation (4) and substitution into (3) gives the rewritten expression (5). In the present case,

$$[(1a)]/([(1a)]_0 - [(1a)]) = k_{ea}/k_1 + k_{ea}k_2/k_{eb}k_1 \quad (5)$$

again neglecting the very small $^{18}O$ isotopic effect, $k_1 = k_2 \equiv k$. Furthermore, the unimolecular escape rate constants for the two esters must of necessity be identical, *i.e.* $k_{ea} = k_{eb} \equiv k_e$, which by introduction in equation (5) gives (6).

$$k = k_e\{[(1a)]_0 - [(1a)]\}/\{2[(1a)] - [(1a)]_0\} = k_e[(1b)]/\{[(1a)] - [(1b)]\} \quad (6)$$

The unimolecular escape rate constant is equal to the reciprocal value of the mean residence time, $\tau$, of the molecule in the reactor,[16] the latter being calculated according to the Knudsen formula [equation (7)], where $V$ is the reactor volume (0.13 cm$^3$) and $A$ is the area of the orifice (0.03 cm$^2$). $\bar{c}$, the mean molecular rate, can be estimated according to the kinetic gas theory [equation (8)], $T$ being the temperature and $M$ the molecular weight of the molecule under investigation, *i.e.* in the present case 76.

$$\tau = 4V/\bar{c}A \text{ s} \quad (7)$$

$$\bar{c} = 1.46 \times 10^4(T/M)^{\frac{1}{2}} \text{ cm s}^{-1} \quad (8)$$

Since the peaks 43 and 45 (Figure 2), arising from (1b) and (1a), respectively, have equal c.a. probabilities,* the intensities of the peaks, $I_{43}$ and $I_{45}$, can be taken as a direct measure of the mutual amounts of (1b) and (1a). On the above basis we are able to rewrite equation (6) as (9), which is directly applicable to the experimental data obtained. Relevant data and the calculated rate constants at the temperatures 1 253 and 1 404 K are given in the Table.

$$k = k_eI_{43}/(I_{45} - I_{43}) = I_{43}/\tau(I_{45} - I_{43}) \quad (9)$$

Intensities of the peaks 43 and 45 in the c.a. mass spectra (*cf.* Figure 2), mean residence times, and unimolecular escape rate constants for $^{18}O$-labelled methyl acetate, and calculated low-pressure rate constants for the (1a) ⟶ (1b) reaction at 1 253 and 1 404 K. The unit for the peak intensities are arbitrary

| $T$/K | $I_{43}$ | $I_{45}$ | $10^4\tau$/s | $10^{-3}k_e$/s$^{-1}$ | $10^{-2}k$/s$^{-1}$ |
|---|---|---|---|---|---|
| 1 253 | 9 | 100 | 2.66 | 3.76 | 3.72 |
| 1 404 | 31 | 100 | 2.52 | 3.97 | 17.8 |

As the thermolyses are carried out in a reactor operating at very low pressure,[9] it is emphasized that the calculated rate constants are low-pressure values. Unfortunately the construction of the reactor used,[9] even fulfilling the requirements for a Knudsen reactor, does not allow us to determine the effective collision frequency. A further disadvantage, from a thermodynamic point of view, is that the Curie Point principle only allows us to operate at a rather limited number of temperatures. Hence, with the present experimental results it is not possible to derive the high-pressure limit Arrhenius parameters for methyl acetate isomerization.

Finally, it should be noted that the above discussion has been carried through on the assumption that isomerization proceeds as a pure unimolecular gas-phase reaction. The possible involvement of a surface catalytic effect, which compared with previous experiments[17] seems rather unlikely, is similarly left for further investigation.

*Conclusions*.—We have by the present study demonstrated thermally induced methyl acetate isomerization in the gas phase at elevated temperatures. The reaction proceeds unimolecularly *via* an electron-delocalized four-membered cyclic transition state through vibrational excitation of the OCO and COC in-plane bending modes of the ester group.

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## REFERENCES

[1] Part 4, L. Carlsen, H. Egsgaard, and D. N. Harpp, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1166; Part 3, L. Carlsen, H. Egsgaard, E. Schumann, H. Mrotzek, and W.-R. Klein, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1557.

[2] S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions,' NSRDS–NBS 21, Washington, 1970, pp. 149—215, and references cited therein; R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1978, 755, 1255; 1979, 1730, as well as previous papers in these series

[3] D. B. Bigley and R. E. Gabbott, *J. Chem. Soc., Perkin Trans. 2*, 1975, 317.

[4] P. C. Oele, A. Tinkelenberg, and R. Louw, *Tetrahedron Lett.*, 1972, 2375.

[5] G. G. Smith, K. J. Voorhees, and F. M. Kelley, *Chem. Commun.*, 1971, 789.

[6] G. G. Smith and J. A. Kirby, *Analyst*, 1969, **94**, 242.

[7] E. I. Leupold and A. Renken, *Chem.-Ing.-Tech.*, 1977, **49**, 667.

[8] P. P. T. Sah, *J. Am. Chem. Soc.*, 1928, **50**, 516.

[9] L. Carlsen and H. Egsgaard, *Thermochim. Acta*, 1980, **38**, 47.

[10] R. G. Cooks, 'Collision Spectroscopy,' Plenum Press, New York, 1978.

[11] C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, 1938, **60**, 2419.

[12] The c.a. mass spectrum of methyl acetate resembles the 70 eV e.i. mass spectrum; S. R. Heller and G. W. A. Milne, 'EPA/NIH Mass Spectra Data Base,' NSRDS–NBS 63, Washington, 1978, vol. 1.

[13] L. Herk, M. Field, and M. Szwark, *J. Am. Chem. Soc.*, 1961, **83**, 2998.

[14] W. O. George, T. E. Houston, and W. C. Harris, *Spectrochim. Acta*, 1974, **30A**, 1035.

[15] J. K. Wilmhurst, *J. Mol. Spectrosc.*, 1957, **1**, 201.

[16] D. M. Golden, G. N. Spokes, and S. W. Benson, *Angew. Chem.*, 1973, **85**, 602.

[17] L. Carlsen, H. Egsgaard, and E. Schaumann, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1206.

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* The c.a. probability of a given ion X in the c.a. mass spectrum of a single ion with mass $M$ is expressed by $I_X/\sum_{1}^{M-1} I_i$ (see L. Carlsen and H. Egsgaard, submitted for publication).