Letters to the Editor

Dear Sir,

Kinetic Energy Release During CO Loss by Rearrangement of α -Acyl Carbenium Ions¹

The loss of CO from acyl ions (reaction (1)) is a well known fragmentation reaction. Williams *et al.* have shown² that the kinetic energy T released during reaction (1) is small (~1 kJ mol⁻¹), but increases (~5 kJ mol⁻¹) if the incipient carbenium ion R rearranges to a more stable ion R' by a 1,2-hydride or 1,2-methyl shift. It is suggested that in the latter case most of T stems from the potential energy released in the exothermic isomerization $[R]^+ \rightarrow [R']^+$ (Scheme 1, reaction (1)). We report here on

$$R \xrightarrow{-CO} \longrightarrow [R^{+} \xrightarrow{-CO}] \longrightarrow R^{+} + CO$$

$$\downarrow Rearrangement \qquad (1)$$

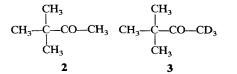
$$R'^{+} \xrightarrow{-CO} R'' \xrightarrow{-CO} R'' + CO$$

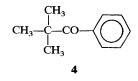
$$R \xrightarrow{-C} \xrightarrow{-CO} R'' \xrightarrow{-O} R \xrightarrow{-C} \xrightarrow{+} + CO \qquad (2)$$

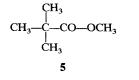
$$R''$$
Scheme 1

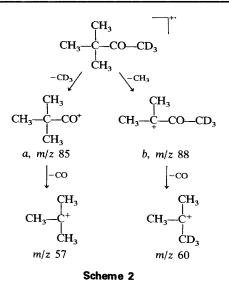
the kinetic energy release during a related rearrangement in α -acyl carbenium ions which fragment to carbenium ions and CO by a 1,2-shift of group R" (Scheme 1, reaction (2)). While metastable [tert-C₄H₉CO]⁺

$$\begin{array}{ccc} CH_3 & CH_3 \\ \downarrow & \downarrow \\ CH_3 - C - CO - C - CH_3 \\ CH_3 & CH_3 \end{array}$$









ions m/z 85 from di-tert-butyl ketone (1) give rise to the expected narrow signal $(T_{0.5} = \approx 10 \text{ meV}, \text{ Fig. 1(a)})$ due to CO loss in the 2nd field free region of a VG ZAB-2F mass spectrometer,³ the m/z 85 ions formed by loss of CH3. from tert-butyl methyl ketone (2) give rise to a flat-topped signal ($T_{0.5} \approx 315 \text{ meV}$) for the same reaction. The investigation of the trideuteromethyl analogue (3) revealed that this unexpected difference in the energy released during the reaction of m/z 85 ions is due to the presence of α -acetyl carbenium ions **b** in addition to trimethylacetyl ions a in the mass spectrum of 2.4 As indicated in Scheme 2 CH₃ and CD₃ are lost from unstable molecular ions $([M-CD_3]/[M-CH_3] =$ 0.4) and metastable molecular ions of $\bf 3$ $([M-CD_3]/[M-CH_3]=0.6)$. Both metastable ions a and b lose CO, the former giving rise to a Gaussian shaped signal in the mass analysed ion kinetic energy (MIKE) spectrum with $T_{0.5} = 16$ meV, the latter giving rise to a dish-shaped peak (Fig. 1(b)) with $T_{0.5} = 365$ meV and $T_h = 135$ meV (measured between the 'horns' of the peak⁵). The elimination of CO from ions b must occur by a rearrangement reaction and is most easily explained by a 1,2-shift of the methyl group. Thus, this fragmentation is a further example of the rule that a large release of kinetic energy is associated with a rearrangement of the reacting ions.

However, there are two fundamental differences between the loss of CO by rearrangement in α -acyl carbenium ions and the rearrangement of acyl ions during CO loss as discussed by Williams et al.² First, the heats of formation of ions a and b are obviously similar, because both ions are formed concurrently from metastable molecular ions of 2 (and 3). Hence, the isomerization $b \rightarrow a$ is not exothermic and cannot be the origin of the kinetic energy additionally released. Of course, the reaction enthalpy for the elimination of CO from a and b is also very similar because the same products are formed. Hence, the increase of the kinetic energy release must be due to the potential energy of the transition state of the rearrangement and at least in the case of ion b the 1,2-methyl shift is associated with a distinct activation energy.

Second, the signals due to loss of CO from acyl ions are Gaussian shaped,² indicating that the excess energy from the exothermic isomerization fluctuates statistically into the reaction coordinates, the

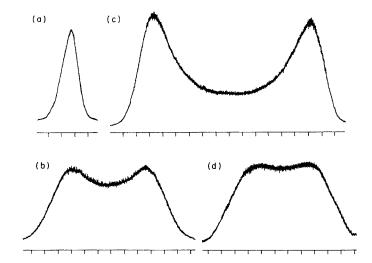
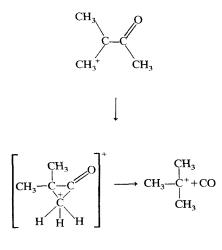


Figure 1. Peak shapes for loss of CO from (a) $(CH_3)_3CCO^+$ (from 1); (b) $(CH_3)_2\overset{+}{C}COCD_3$ (from 3); (c) $(CH_3)_2\overset{+}{C}COOCH_3$ (from 5); (d) $(CH_3)_2\overset{+}{C}COO_6H_5$ (from 4).

isomerization taking place in a weakly bonded complex between a (rearranging) carbenium ion and a CO molecule. In contrast, the dish-shaped peak for the CO elimination from metastable ions b and other α -acyl carbenium ions (see below) indicates a non-statistical distribution of the released kinetic energy and that the process is always associated with the release of kinetic energy $(T_{\min} \approx T_h^5)$. Although no exact description of the process can be given without knowledge of the potential energy hypersurface of the system, it is likely that the transition state of the 1,2-methyl shift of ions b (probably resembling a 'corner' protonated dimethyl cyclopropanone) collapses directly to the products, bypassing the trimethylacetyl ion (Scheme 3). The loss of



Scheme 3

Dear Sir,

The Use of the Abbreviation MS/MS

The International Union of Pure and Applied Chemistry has recently recommended¹ that the use of the initials MS should be limited to the term GC/MS to indicate the coupling of a gas chromatograph to a mass spectrometer and that, otherwise, the initials MS should not be used in mass spectrometry (MS) papers, because their use can be confusing. The American Society for Mass Spectrometry (ASMS) has recently re-established its Nomenclature Committee to advise, *inter alia*, on the use of initials as abbreviations.

The situation is somewhat confused because the term 'mass spectrometer' (MS) is used to describe magnetic sector (ms) instruments which should, properly, be described as 'momentum spectrometers' (m.s.). Further, when mass spectroscopists (ms) use ms m.s. to study metastable (ms) ions, they

Table 1. Kinetic energy release (meV) associated with loss of CO from (CH₂)₂C--CO--R" ions^a

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R″	T _{0.1}	T _{0.2}	T _{0.5}	T _{0.8}	Th
CD ₃ -	610	595	365	255	135
C ₆ H ₅	705	640	410	260	120
CH₃O-	1250	1160	990	855	680
<u> </u>					

^a For definition of T_x see Ref. 5.

CO from α -acyl ions by a 1,2-group shift is not restricted to the migration of a methyl group. The $[M-CH_3]^+$ ions m/z 147 in the mass spectrum of tert butyl phenyl ketone (4) lose a CO molecule via migration of a phenyl group. The signal observed for this reaction of metastable m/z 147 ions is flattopped (Fig. 1(d)) and the corresponding T values are similar to those for CO loss from ions b (Table 1). Similarly, elimination of CO via 1,2-migration of a CH₃O- group is observed for metastable [M-CH₃]⁺ ions in the mass spectrum of m/z = 101trimethylacetic acid methyl ester (5). The signal obtained for this process (Fig. 1(c)) is beautifully dish-shaped and corresponds to a large amount of kinetic energy released in a non-statistical manner (Table 1). The thermochemistry of the relevant ions in the mass spectra of 2, 4 and 5 is not yet known. Hence, no decision can be made at present as to whether the increase of T values for reaction (2) in the series $R' = -CH_3$, $-C_6H_5$, -OCH₃ reflects an increase of the activation energy for a 1,2-drift of these groups or a decrease in the reaction enthalpies of these processes.

often use multiple scans (MS) to obtain adequate signal-to-noise ratio. Some of the most senior Ms ms have gone against the International Union of Pure and Applied Chemistry's recommendation and are using the terms 'MS/MS' and 'ms/ms' to apply to a technique that can be used with certain multi-sector (M.S.) instruments.

Jargon of this kind is likely to become widespread if Editors of Journals, such as Organic MS do not insist that individual ms avoid the use of initials whenever possible and particularly when their use is contrary to the recommendations of our international body dealing with nomenclature in MS.

After all, it does not take long, only a few thousand ms,² to replace a sentence littered with initials by one written in simple English. It is my opinion, and that of many scientists (**m.s.**), that the indiscriminate use of initials in scientific manuscripts (sm) must stop! (**M.S.**)

Yours HANS-FRIEDRICH GRÜTZMACHER, ANNE-MARIE DOMMRÖSE and ULRICH NEUERT Fakultät für Chemie, Universität Bielefeld, BRD 4800 Bielefeld 1, West Germany March 1981

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- D. H. Williams, B. J. Stapleton and R. D. Bowen, *Tetrahedron Lett.* 2916 (1978).
- Temperature of inlet system and ion source, 200 °C; electron energy, 70 eV; accelerating voltage, 6 kV; ion source pressure, 10⁻⁶ Torr; analyser pressure, 3×10⁻⁹ Torr.
- 4. This is also seen from the MIKE spectra of various ions at m/z85. The MIKE spectrum of m/z85 ions from 1 contains only one signal due to loss of CO, and that of m/z85 ions from 2 shows additional peaks for product ions m/z67 (85–H₂O) and m/z43 (85–C₃H₆). These product ions, shifted by 3 mass units, appear also in the MIKE spectrum of $[M-CH_3]$ + ions of 3.
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Yours most sincerely (MS)

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Editor's Note: Ms is also used to indicate a female person of indeterminate marital status—Editor-in-Chief.

Publisher's Note: MS is manuscript in publishing parlance.