Geometrical Inversion of Methoxymethyl Cations

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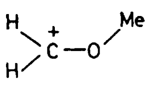
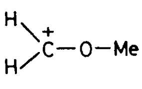
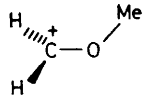
Summary The barrier for geometrical isomerization of the title ion [$\Delta H^{\ddagger} = 11{\cdot}9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -4$ cal mol^{-1} K^{-1} (1 cal = 4·184 J), variable temperature n.m.r. spectrum 270 MHz] agrees with *ab initio* (4-31G) calculations for an inversion process ($\Delta E_{\mathrm{calc}} = 12{\cdot}0$ kcal mol^{-1}); the values computed for a rotation around the C$^+$–O bond (20·8 kcal mol^{-1}) or at the STO-3G level (25·2 and 32·8 kcal mol^{-1}, respectively) are too high.

STABILIZATION by the α-oxygen makes the methoxymethyl cation (**1**) observable in superacid solution.[1] Its salts have even been isolated as solids[2a] and used as initiators for cationic polymerizations.[2b] *Ab initio* M.O. calculations[3] predict that the planar form (**1a**) of this primary carbocation is more stable than the secondary isopropyl cation. At the same time, the calculations predict that (**1a**) should undergo geometrical isomerization by inversion (**1b**) rather than by rotation around the C$^+$–O bond. In fact, the perpendicular form (**1c**) relaxes to the linear form (**1b**) upon optimization of the C–O–C angle.[3] (The relative energies are given under the formulae.)



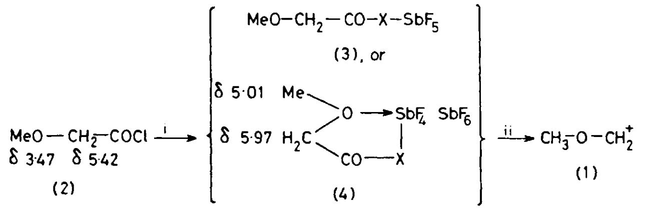




	(**1a**)	(**1b**)	(**1c**)
STO-3G:	0	25·2	32·8† kcal mol^{-1}
4-31G:	0	12·0	20·8† kcal mol^{-1}

While the results obtained at the STO-3G and 4-31G levels[4] are in qualitative agreement, the values for the relative energies at the two levels are significantly different. Fortunately, these calculations are amenable to experimental verification as the 4-31G value implies that the inversion of (**1**) be observable below room temperature, while the STO-3G result requires (**1a**) to be geometrically stable at significantly higher temperatures.

Cation (**1**) is conveniently prepared from methoxyacetyl chloride (**2**)[1,3] and SbF$_5$, in SO$_2$FCl at −75 °C. A complex is formed which can be formulated as (**3**) or more probably (**4**),** based on its ^{1}H n.m.r. spectrum, indicated on the formulae. (The structure of an acyl cation proposed for this species[1] is contradicted by the ^{13}C n.m.r. spectra.‡) Decarbonylation occurs between −30 and −10 °C, forming (**1**).



SCHEME. Reaction conditions, i SbF$_5$–SO$_2$FCl, −75 °C, ii −CO, heat. X = Cl or F.

In the ^{1}H n.m.r. spectrum of (**1**) at 60 MHz and −60 °C, the two hydrogens at C-1 have the same chemical shift.[1a] At 100 MHz, previous authors could analyse the CH$_2$ signal as an AB pattern by computer simulation of the peak.[1b] In our hands, the broad CH$_2$ signal ($W_{\frac{1}{2}}$ 7·4 Hz at −65 °C) was not satisfactorily resolved for a variable temperature study at 100 MHz, although it narrowed on warming.

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† The relative energy given for (**1c**) was calculated with the C–O–C angle held at the value found optimum for (**1a**) (128·5°); 1 cal = 4·184 J.

** Alternatively, a referee suggested the structure $\mathrm{MeO^{+}.CH_2.CO}$ for the intermediate. This possibility cannot be discounted, but the structure seems highly strained.

‡ The chemical shift of the CO signal moves 38 p.p.m. downfield upon reaction with SbF$_5$,[3] as expected for (**3**) or (**4**).[5] In the formation of an acyl cation from the acid chloride this peak should move upfield.[5]

The peak (δ 9·61) was eventually resolved at 270 MHz;[§] a clean AB pattern ($\Delta\delta$ 34·5 Hz, J 20·7 Hz) was obtained at −64·4 °C. This was temperature dependent, becoming a singlet at +1·0 °C (Figure), while cooling to −74·6 °C did not alter the spectrum. The lines were somewhat broadened by allylic coupling[1a] with the Me protons (δ 5·56), but no further splitting was observed at all temperatures. The rates of exchange were determined at six temperatures[¶] by line shape analysis.[6] From these rates the activation parameters: $\Delta H^{\ddagger} = 11{\cdot}9 \pm 1{\cdot}2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -4 \pm 3$ kcal mol^{-1} K^{-1} were calculated. The uncertainties quoted represent the uppermost limits based on the experimental errors, not statistically derived quantities.

In conclusion, our experiments substantiate the inversion barrier calculated at the 4-31G level; the STO-3G value is too high. The experiments thus lend weight to the prediction that the preferred pathway for geometrical isomerization of (**1a**) is the inversion at oxygen,[7] rather than rotation around the C$^+$–O bond as considered previously.[8]

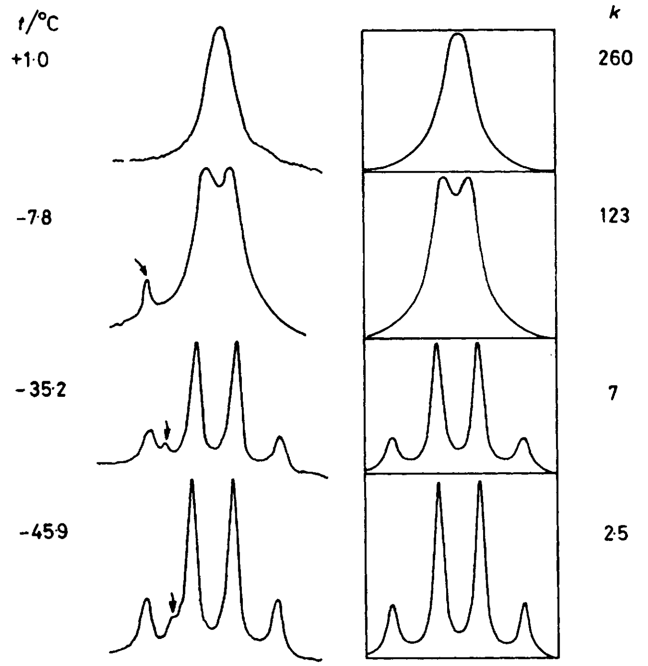

FIGURE. Recorded (left) and simulated (right) ^{1}H-n.m.r. signals for the methylene group of (**1**), in the temperature range of measurable exchange rates. (The arrows mark the signal of an impurity, probably H_3O^+).

(*Received*, 23*rd August* 1979; *Com.* 905.)

[§] The instruments used were: Varian A60 (60 MHz), Varian XL-100 (100 MHz), and Brucker HX-270 (270 MHz). Me_4Si in CD_2Cl_2 (external) provided the reference and lock signal, respectively.

[¶] −45·9 °C (2·5 ± 0·25), −35·2 (7 ± 0·7), −25·9 (28 ± 2), −17·1 (52 ± 2), −7·8 (12·3 ± 3), and +1 (260 ± 26). To decrease the vapour pressure, *ca.* 15% FSO_3H by volume was added to the sample for the +1 °C measurement. The uncertainty in temperature was no greater than 1 °C, probably closer to 0·5 °C. The chemical shifts were slightly temperature dependent; at +1·0 °C $\Delta\delta$ was 32·8 Hz. This variation was taken into account in the line-shape analysis.

[1] (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1967, **89**, 2993; (b) A. M. White and G. A. Olah, *ibid.*, 1969, **91**, 2943.

[2] (a) V. Jaacks, H. Frank, E. Grünberger, and W. Kern, *Makromol. Chem.*, 1968, **115**, 290; G. A. Olah and J. J. Svoboda, *Synthesis*, 1973, 52; B. A. Komarov, B. A. Rozenberg, and N. S. Erikolopyan, *Izvest. Akad. Nauk S.S.R.*, 1974, 1874; (b) A. Ciaperoni, G. B. Gechele, and L. Mariani, *J. Polymer Sci., Part A*-1, 1967, **5**, 891; B. A. Komarov, A. T. Ponomarenko, V. P. Volkov, B. A. Rozenberg, and N. S. Erikolopyan, *Vysokomol. Soedinenina, Ser. A*, 1974, **16**, 2464, and previous papers.

[3] D. Fărcaşiu and J. A. Horsley, to be published.

[4] The calculations were performed with the Gaussian 70 series of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Q.C.P.E., Indiana University, Bloomington, Indiana.

[5] G. A. Olah, A. Germain, and H. C. Lin, *J. Amer. Chem. Soc.*, 1975, **97**, 5481.

[6] The calculations of the line shapes for the AB system were carried out using a program kindly supplied by Professor Martin Saunders.

[7] Similar predictions were made by recent calculations on protonated formaldehyde (F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Canad. J. Chem.*, 1975, **53**, 1144), while previous calculations had predicted the contrary (P. Ros, *J. Chem. Phys.*, 1968, **49**, 4902). The intervention of proton exchange with the acid prevented the experimental verification of these predictions for CH_2OH^+.

[8] W. P. Meyer and J. C. Martin, *J. Amer. Chem. Soc.*, 1976, **98**, 1231.