Carbonium Ion Rearrangement in the Crystalline State: Isokinetic 'Phase' Point

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An isokinetic point has been found for the degenerate rearrangement of heptamethylbenzenium tetrachloroaluminate on passing from the solution to the crystalline state.

Carbonium ion rearrangements are interesting both from theoretical and synthetic points of view. Although considerable advances have been made in the studies of stereochemistry, structure–reactivity relationships, and medium effects in such reactions proceeding in the liquid phase,[1,2] the solid-state effects are not clear so far.

In the course of our studies of phase-state effects on carbonium ion rearrangements, we have found that the rates of 1,2-shifts in long-lived carbocations do not change significantly on passing from the liquid to the 'frozen' solidified solution[3] (*cf.* ref. 4), but change greatly on passing to the crystalline state.[5] It is very interesting that the rigid ionic environment in the crystal should exert a strong influence over the rearrangements.

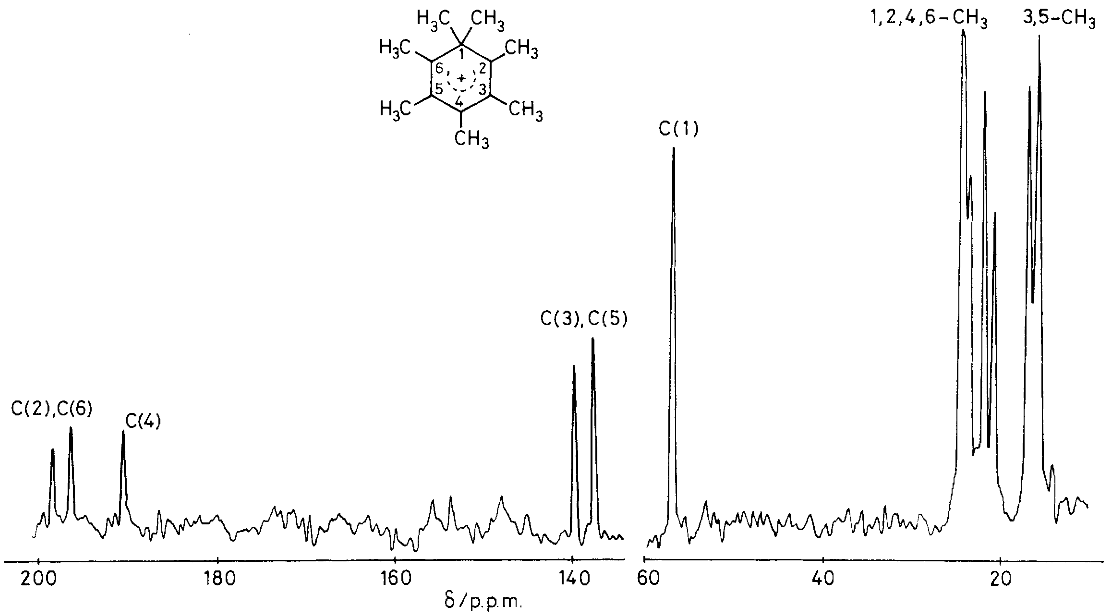
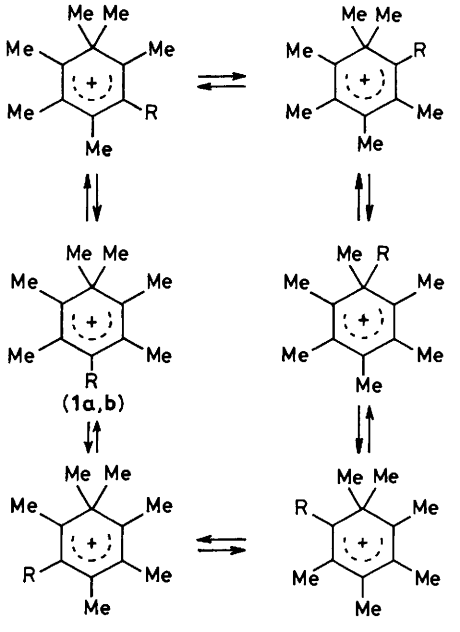


Figure 1. ^{13}C C.p.m.a.s. n.m.r. spectrum (CXP-300, Bruker) of heptamethylbenzenium tetrachloroaluminate at 20 °C. The carbon shift of the C(1) atom is taken to be δ 56.6 p.p.m. from Me_4Si (*cf.* ref. 2).



Scheme 1. a, R = Me; b, R = CHD_2.

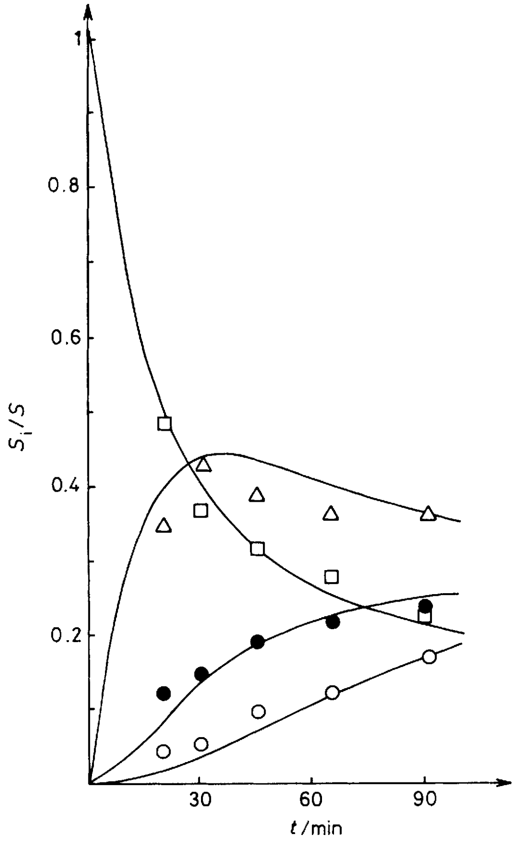


Figure 2. ^{2}H N.m.r. relative intensities (S_i/S) of methyl signals *vs.* the reaction time (t) for the 1,2-methyl shift at 0 °C. The solid curves represent the theoretical relationships, the points represent the experimental data (○ S_{gem}/S, ● S_{ortho}/S, △ S_{meta}/S, □ S_{para}/S; $S = S_{gem} + S_{ortho} + S_{meta} + S_{para}$).

As a continuation of our investigation of solid-state effects on intramolecular carbocation rearrangements, we have studied the kinetics of the degenerate rearrangement of the heptamethylbenzenium ion (**1**) in the crystalline state. The tetrachloroaluminate salt of (**1**) has been prepared by the reaction of 1-methylene-2,3,4,4,5,6-hexamethylcyclohexa-2,5-diene[6] with $HAlCl_4{\cdot}2Et_2O$[7] in CH_2Cl_2 at −90 °C (*cf.* ref. 8). Addition of dry ethyl acetate at −78 °C to the solution gave yellow needles, m.p. 94—95 °C. The ^{13}C cross polarisation magic-angle spinning (c.p.m.a.s.) n.m.r. spectrum of the crystals is very similar to that obtained by Lyerla *et al.*,[4] except that a somewhat greater inequivalence of the methyl carbon signals is observed (Figure 1).

It is reasonable to expect the ion (**1**) in the crystalline state to undergo six-fold degenerate rearrangement by a series of 1,2-shifts of the methyl groups attached to the cyclohexadi-

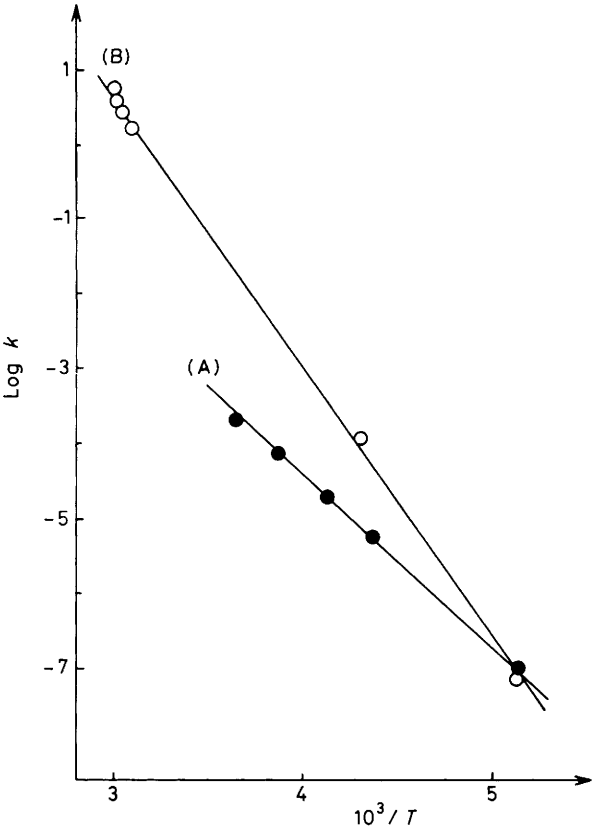


Figure 3. Plots of log *k* against $1/T$ for the degenerate 1,2-methyl shift in heptamethylbenzenium tetrachloroaluminate; crystalline state (A), solution in CH_2Cl_2 (B).

enyl ring relative to one of the two geminal methyl groups (*cf.* refs. 2, 5, and 9). Indeed, when the salt of the ion (**1b**) remains in the crystalline state at 0 °C, redistribution of the intensities of signals in ^1H and ^2H n.m.r. spectra is observed.† The dynamics of redistribution is in good agreement with that calculated for the intramolecular mechanism of the 1,2-shift (Scheme 1 and Figure 2), with some inequivalence of the two geminal methyl groups[8] and of the C(2) and C(6) atoms,[4] and isotopic effects being neglected.

The rate constants for the 1,2-methyl shift were obtained at temperatures ranging from -78 to 0 °C. Least-squares treatment of the data gave the following values for the Arrhenius parameters: $E_a = 44.0 \pm 0.8$ kJ mol^{-1}, log $A = 4.8 \pm 0.2$. These values are much lower than those obtained from the solution of heptamethylbenzenium tetrachloroaluminate in CH_2Cl_2, *i.e.*, $E_a = 69.2 \pm 0.6$ kJ mol^{-1}, log $A = 11.5 \pm 0.1$. A striking feature of the respective plots shown in Figure 3 is the presence of a isokinetic 'phase' point (at -77 °C). A decrease in the activation energy for the 1,2-methyl shift in the crystalline state may result from electrostatic interaction between the partial positive charge on the 'migrating' (actually fixed) methyl group and the neighbouring $AlCl_4^-$ anions in the transition state. A decreased activation entropy (at 0 °C, $\Delta S^\ddagger = -160.6$ *vs.* $\Delta S^\ddagger = -32.4$ J K^{-1} mol^{-1} for solution) may be due to the much more limited atomic motions in the transition state of the rearrangement in a crystalline lattice.

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References

1 M. Saunders, J. Chandrasekhar, and P. von R. Schleyer, in 'Rearrangements in Ground and Excited States,' vol. 1, ed. P. de Mayo, Academic Press, New York, 1980, p. 1.
2 V. A. Koptyug, 'Arenonium Ions. Structure and Reactivity,' Nauka, Novosibirsk, 1983.
3 G. I. Borodkin, Ye. B. Panova, and V. G. Shubin, Abstracts of Papers for the All-Union Conference on Low Temperature Chemistry, Moscow State University Press, Moscow, 1979, p. 68.
4 J. R. Lyerla, C. S. Yannoni, and C. A. Fyfe, *Acc. Chem. Res.*, 1982, **15**, 208.
5 G. I. Borodkin, S. M. Nagy, and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2639.
6 W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, 1958, **4**, 178.
7 N. M. Alpatova, V. V. Gavrilenko, Yu. M. Kessler, O. R. Osipov, and D. N. Maslin, 'Complexes of Hydride and Halide Metalloorganic Compounds of Aluminium,' Nauka, Moscow, 1970, p. 98.
8 N. C. Baenziger and A. D. Nelson, *J. Am. Chem. Soc.*, 1968, **90**, 6602.
9 A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, *Inorg. Chem.*, 1976, **15**, 1326.

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† The salt was dissolved in CH_2Cl_2 at -80 °C and a ^1H or ^2H n.m.r. spectrum of the solution was recorded.