Gas-phase Conformational Preference of the Methyl Group from Equilibration of 1-, 3-, and 4-Methyldiamantane on a Chlorinated Platinum–Alumina Catalyst

By R. Hamilton, D. E. Johnston, M. A. McKervey,* and J. J. Rooney
(*Department of Chemistry, The Queen's University, Belfast* BT9 5AG)

Summary On a chlorinated platinum–alumina catalyst/hydrogen chloride co-catalyst, the isomeric methyldiamantanes establish equilibrium, the temperature dependence of which yields a value of 2·14 kcal mol^{-1} for the gas-phase conformational enthalpy of the methyl group.

Recent work[1] has indicated that equilibration studies with monosubstituted diamantanes can be applied in a useful way to an important problem in physical organic chemistry, that of measuring the conformational preferences of some cyclohexyl derivatives. The method presupposes that 1- and 4- substituted diamantanes, *e.g.* (**1**) and (**2**), are formally analogous to the axially and equatorially substituted chair conformations of a monosubstituted cyclohexane, and a requisite for its use is that equilibria between monosubstituted diamantanes can in fact be established chemically. This was achieved *via* an intermolecular hydride transfer mechanism for the alcohols,[1] chlorides[2] and bromides.[3] The conformational enthalpies measured for these substituents are believed to be as reliable as those obtained in the liquid phase by other methods, are qualified by different reservations, yet agree well with them. An important aspect of this approach is that it can be extended to gas-phase studies as we now illustrate with a direct determination of the conformational enthalpy of the methyl group.

Equilibration of 1- and 4-methyldiamantane, (**1**)[4] and (**2**),[5] was established rapidly between 433 and 585 K on chlorinated platinum–alumina. This material is known to be an effective catalyst for gas-phase adamantane rearrangements, particularly when hydrogen chloride is employed as co-catalyst.[6] The mechanism probably involves a skeletal reorganisation of the type proposed for the interconversion of 1- and 2-methyladamantane.[7] The procedure consisted of passing the isomers over the catalyst in a stream of hydrogen chloride. Equilibrium constants at several temperatures were measured by g.l.c. (see Table).† Substantial amounts of 3-methyldiamantane (**3**)[8] were also present at equilibrium with isomers (**1**) and (**2**); consequently, the thermodynamic data, derived from the temperature dependence of the equilibrium by linear least-squares analysis, are presented in the Scheme as a ternary system, thereby illustrating the consistency of the method. Included in parenthesis are theoretical entropy changes,

Table. *Equilibration data for isomers* (**1**), (**2**), *and* (**3**).

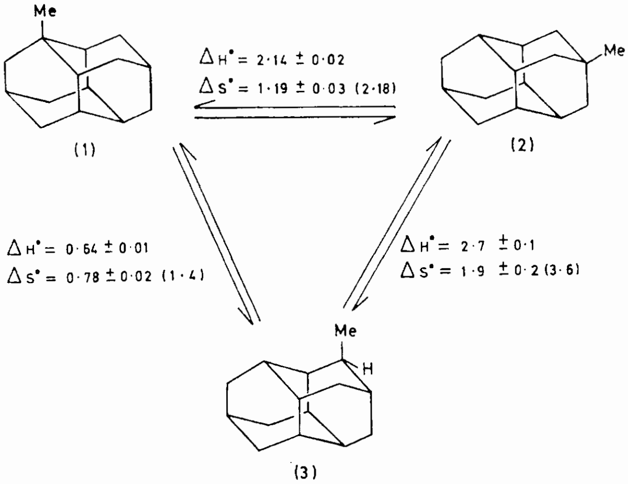
	T/K	433	443	473	503	545	573	583	585
ln$K$,	(3)→(1)	0·35	0·34	—	0·25	0·20	0·17	0·16	—
ln$K$,	(1)→(2)	1·88	1·84	1·68	1·54	—	1·28	1·25	1·24
ln$K$,	(3)→(2)	2·21	2·08	—	1·72	1·50	1·42	1·39	—

---

† The equilibrium ratios were measured separately for each pair of isomers.

calculated from the different symmetry numbers of the three isomers[1] and from the entropy of mixing of (**3**).

The data reveal that isomer (**3**) is of highest energy because of the secondary character of the methyl group and its axial disposition with respect to one cyclohexane ring of the skeleton.[9] Isomer (**2**) is of lower enthalpy than isomer (**1**) by 2·14 kcal mol^{-1}. This value for the conformational enthalpy of the methyl group is in remarkably good agreement with the carefully measured gas-phase thermochemical value of 1·91—1·96 kcal mol^{-1}, obtained from differences of heats of combustion of *cis*- and *trans*-1,3- and 1,4-dimethylcyclohexane.[10] It is also in complete accord with the only other recorded gas-phase value of 2·0—2·1 kcal mol^{-1} derived from equilibration of the isomeric 1,3,5-trimethylcyclohexanes.[11] This agreement reinforces the view[1] that despite the large differences in flexibility between the two systems, diamantyl derivatives provide excellent models for studying some aspects of conformational change in substituted cyclohexanes. Agreement between the measured and calculated entropy changes is less satisfactory, possibly because interference with methyl group rotation has not been taken into account.[10b]



Scheme. ΔH° *in kcal mol*$^{-1}$; ΔS *in cal mol*$^{-1}$ *deg*$^{-1}$. *The thermodynamic data relate to the direction indicated by the outer of the two arrows in each case.*

Chlorinated platinum–alumina is a very effective catalyst for these equilibrations in solution[12] and further studies to obtain the difference between the gas-phase and liquid-phase conformational enthalpies of the methyl group are in progress.

We thank the Northern Ireland Ministry of Education for a postgraduate grant (to D.E.J.).

(*Received*, 31*st July* 1972; *Com.* 1333.)

---

[1] D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J.C.S. Chem. Comm.*, 1972, 29.

[2] M. A. McKervey, D. E. Johnston, and J. J. Rooney, *Tetrahedron Letters*, 1972, 1547.

[3] The value measured for the bromo-substituent was 0·59 kcal mol^{-1}, see T. Courtney, D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J.C.S. Perkin I*, in the press.

[4] E. Osawa, Z. Majerski, and P. von R. Schleyer, *J. Org. Chem.*, 1971, **36**, 205.

[5] Although isomer (**2**) can be prepared by rearrangement of *exo*-tetrahydrotricyclopentadiene (see ref. 8), it is more conveniently obtained by the Grignard coupling procedure described in ref. 4.

[6] D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Amer. Chem. Soc.*, 1971, **93**, 2798.

[7] Z. Majerski, P. von R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5731.

[8] T. M. Gund, M. Nomura, V. Z. Williams, jun., P. von R. Schleyer, and C. Hoogzand, *Tetrahedron Letters*, 1970, 4875.

[9] Δ*H*° for equilibration of 1- and 2-methyladamantane is −3·37 kcal mol^{-1} in the liquid phase. This value does not correspond directly to the conformational preference of the methyl group because of the difference in substitution pattern of the two isomers; see E. M. Engler, K. R. Blanchard, and P. von R. Schleyer, *J.C.S. Chem. Comm.*, following communication.

[10] (a) J. A. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand., Sect. A.*, 1947, **39**, 523; J. Prosen, W. H. Johnson, and F. D. Rossini, *ibid.*, 1947, **39**, 173; (b) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488.

[11] C. J. Egan and W. C. Buss, *J. Phys. Chem.*, 1959, **63**, 1887.

[12] R. Hamilton, unpublished observations.