Tetrahedron Letters No.56, pp. 4941-4944, 1969. Pergamon Press. Printed in Great Britain.

INTERCONVERSION OF 2-exo- AND 2-endo-NORBORNYL OXOCARBONIUM IONS VIA THE NORBORNYL CATION. THE FREE-ENTHALPY DIAGRAM(1)

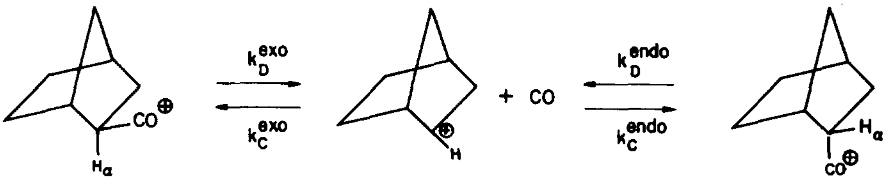
H. Hogeveen and C.F. Roobeek

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.)

(Received in UK 29 October 1969; accepted for publication 4 November 1969)

In a previous report we showed that carbonylation of the norbornyl cation 1 in strongly acidic solutions at room temperature affords the 2-exo-norbornyl oxocarbonium ion 2 exclusively(2). The equilibrium constant $K = \frac{[RCO^{\oplus}]}{[R^{\oplus}][CO]}$ for this reaction was found to be 10^4 $l.mole^{-1}$ at 20 °C. This value is of the same order as those of the 1-adamantyl ion ($K = 2 \times 10^4$ $l.mole^{-1}$) and the t-butyl ion ($K = 7 \times 10^2$ $l.mole^{-1}$), from which fact it was concluded that there is strong evidence for the norbornyl cation to be unusually stabilized ("non-classical" ion).

We now present additional results of the carbonylation of the norbornyl ion, which show that the reported formation of 2-exo-norbornyl oxocarbonium ion 2 is kinetically controlled, and that under thermodynamically controlled conditions 2-endo-norbornyl oxocarbonium ion 3 is formed to the same extent (ratio 2 : 3 = 51 : 49).



2 1 3

The interconversion of $\underline{2} \rightleftarrows \underline{3}$ in $FHSO_3$-SbF_5 (1/1 m/m) solution was studied kinetically in the temperature range of 75-102 °C by integration of the NMR multiplets due to protons H_α (in ion $\underline{2}$ at 3.80 ppm(2), and in ion $\underline{3}$ at 4.06 ppm from TMS) at appropriate intervals. During this interconversion, which obeys first-order kinetics to about 80-90% conversion, the intermediate norbornyl ion $\underline{1}$ was not observed. The results are given in the Table.

Table

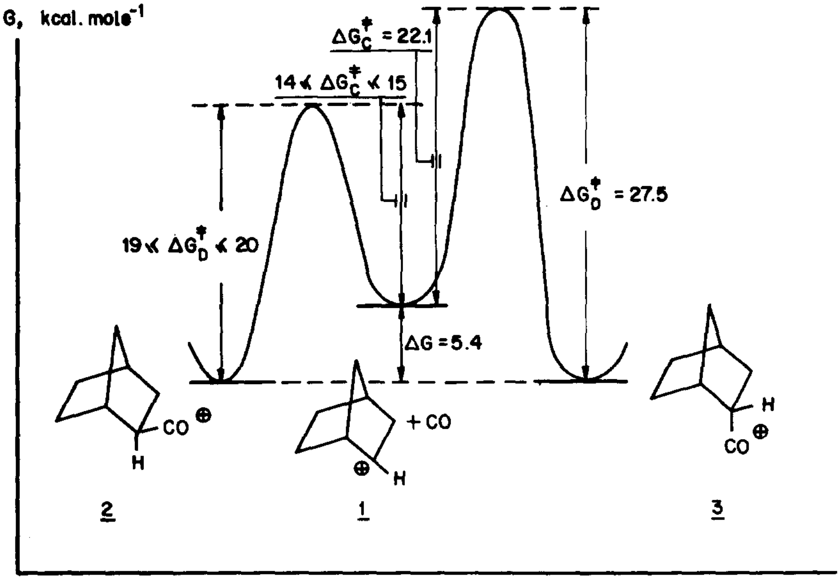
RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE INTERCONVERSION

2-exo-NORBORNYL OXOCARBONIUM ION $\underline{2} \rightleftarrows$ 2-endo-NORBORNYL OXOCARBONIUM ION $\underline{3}$

Temperature, °C	$k^* \cdot 10^4$, s^{-1}	
75	1.53	$\Delta H_D^{\ddagger}$ (endo) = 31.3 $kcal.mole^{-1}$ $\Delta S_D^{\ddagger}$ (endo) = 13 $cal.degree^{-1}.mole^{-1}$ $\Delta G_D^{\ddagger}$ (endo) = 27.5 $kcal.mole^{-1}$ at 20 °C
87.5	7.8 9.0	
94.5	16	
102	38	

$* \ k = k_D^{endo} = k_D^{exo} \cdot k_C^{endo}/k_C^{exo}$.

From the following data the free-enthalpy diagram of the system $\underline{2} \rightleftarrows \underline{1} + CO \rightleftarrows \underline{3}$ can be constructed (see Figure).



Free-enthalpy diagram at 20° and [CO] in $mole.l^{-1}$ for the system 2-exo-norbornyl oxocarbonium ion $\rightleftarrows$ 2-norbornyl ion + CO $\rightleftarrows$ 2-endo-norbornyl oxocarbonium ion in $FHSO_3/SbF_5$ (1 : 1 m/m).

i. Since $k_C^{endo} \ll k_C^{exo}$, $\Delta G^{\ddagger}$ (3 $\longrightarrow$ 2) is equal to $\Delta G_D^{\ddagger}$ (*endo*) (see Table);

ii. from the equilibrium constant k_C^{exo}/k_D^{exo}(2) the free-enthalpy difference $\Delta G = -G(2) + G(1) + G(CO)$ is calculated to be +5.4 kcal.mole^{-1} at 20° and [CO] in mole.l^{-1};

iii. the height of the free-enthalpy barrier in the reaction 2 $\rightleftarrows$ 1 + CO can be put between narrow limits, because (a) the rate of carbonylation in $FHSO_3$-SbF_5-SO_2ClF (1 : 1 : 2 v/v) solution at -60° and 1 atm of CO - [CO] = 0.03 mole.l^{-1} - is too fast for kinetic measurements, which implies $k_C^{exo} \geq 4.10^{-1}$ l.mole^{-1}.s^{-1} and $\Delta G_C^{\ddagger}$ (*exo*) $\leq$ 13 kcal.mole^{-1} at -60° and [CO] = 1 mole.l^{-1}. As the entropy of activation $\Delta S_C^{\ddagger}$ (*exo*) is unlikely to exceed -20 cal.degree^{-1}.mole^{-1}, it follows that $\Delta G_C^{\ddagger}$ (*exo*) $\leq$ 15 kcal.mole^{-1} at +20°; (b) no line-broadening was observed at +60° under equilibrium conditions of the process 2 $\rightleftarrows$ 1 + CO(2), which implies that $k_D^{exo} \leq 10$ s^{-1} and $\Delta G_D^{\ddagger}$ (*exo*) $\geq$ 18.4 kcal.mole^{-1} at +60°. If $\Delta S_D^{\ddagger}$ (*exo*) is taken equal to $\Delta S_D^{\ddagger}$ (*endo*) (13 cal.degree^{-1}.mole^{-1}; see Table), one calculates $\Delta G_D^{\ddagger}$ (*exo*) $\geq$ 19 kcal.mole^{-1} at +20°.

The diagram of the interconversion of *endo*- and *exo*-norbornyl oxocarbonium ions occurring via the norbornyl ion is similar to the diagrams of the solvolysis of *endo*- and *exo*-norbornyl derivatives ("Goering-Schewene" diagram(3)). In solvolysis work the free enthalpy of activation for the reaction of the norbornyl ion with the nucleophile is not known, whereas in our system the complete free-enthalpy picture can be given. The diagram shows that the preferred formation of 2-*exo*-norbornyl oxocarbonium ion 2 from norbornyl ion 1 and CO is due to the same difference in free-enthalpies of the *endo*- and *exo*-transition states that governs the preferred decarbonylation of the *exo*-ion 2.

The effects which determine the free-enthalpy picture are both of a steric and an electronic nature. The steric effects are made evident by the rate of formation of ion 2 (k_C^{exo}) which - although being much larger than that of ion 3 (k_C^{endo}) - is at least 10^2 times lower than those of oxocarbonium ions from t-butyl, t-pentyl and 1-adamantyl(2). Such steric effects are likely to operate in the transition state if a considerable degree of sp^2-hybridization is retained at carbon atom 2, while they do not occur in the initial (ion 1) and final state (ion 2). They will certainly play a more important role in the formation of the *endo*-isomer 3 (or its decarbonylation) than in that of the *exo*-isomer 2 (or its decarbonylation) because of the repulsion of the *endo*-H at carbon atom 6(4) and the --C$\equiv$O group.

The electronic effects which play a role in the free-enthalpy picture are inherent in the non-classical character of the norbornyl ion. Conclusive evidence for the stable, long-lived norbornyl ion to have non-classical stabilization has recently been presented on the basis of chemical reactivity(2,5) and spectroscopy(6). The question to what extent this stabilization is responsible for the difference in free enthalpies of the *endo*- and *exo*-transition states, as in the solvolysis of 2-*endo*- and 2-*exo*-norbornyl derivatives(7), cannot be answered at present.

REFERENCES

1. Chemistry and Spectroscopy in Strongly Acidic Solutions. XXXIII. Part XXXII, H. Hogeveen, J. Lukas and C.F. Roobeek, Chem. Comm. 1969, 920.
2. H. Hogeveen, F. Baardman and C.F. Roobeek, Rec. Trav. Chim., submitted for publication.
3. H.L. Goering and C.B. Schewene, J. Am. Chem. Soc. 87, 3516 (1965); H.C. Brown and M.H. Rei, ibid. 90, 6216 (1968).
4. Compare H.C. Brown, Chem. in Britain 2,199 (1966).
5. H. Hogeveen, Rec. Trav. Chim., submitted for publication.
6. G.A. Olah and A.M. White, J. Am. Chem. Soc. 91, 3954, 3956 (1969).
7. G.D. Sargent, Quart. Revs. 20, 301 (1966).