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Reactions of 1,1,3,3-Tetramethylcyclobutane on Evaporated Metal Films

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Reactions of 1,1,3,3-tetramethylcyclobutane (TMCB)–hydrogen mixtures on evaporated metal films have shown that both ring scission to 2,2,4-trimethylpentane (TMP) and ring enlargement to 1,1,3-trimethylcyclopentane (TMCP) are dominant on sintered platinum films, while ring scission to TMP predominates on sintered palladium and on unsintered molybdenum films. Unsintered tantalum and molybdenum films gave a large production of iC_4 hydrocarbon, particularly above *ca.* 500 K: ring enlargement was a minor reaction found particularly with tantalum. The homogeneous reaction of TMCB giving a large iC_4 production sets in at 600 K. The possibility, suggested by the product distribution, that the reaction of TMCB on Mo and Ta is a metal-assisted free-radical reaction is examined. While it may not be completely excluded that the catalysed ring enlargement on Pt and Pd is a free-radical reaction it is argued that only the previously proposed Rooney–Samman bond-shift mechanism accommodates without added qualifications published facts on bond shifts, including those at quaternary carbon atoms, and also ring enlargements.

Ring enlargement of hydrocarbons on platinum metals has attracted less study than have other hydrocarbon skeletal reactions. An earlier debate centred on whether ring enlargement of methylcyclopentane on platinum takes place by ring opening to a C_6 chain followed by 1,6-ring closure yielding benzene/cyclohexane or whether the reaction is simply a bond shift in which bond switching occurs in a single catalysed step.[1] A programme of ^{13}C-labelling experiments concluded that the former route makes a contribution.[2] The mechanism of the bond-shift reaction for acyclic alkanes is now substantially agreed.[3–5]

A number of experimental observations may be cited as arguments against a mechanistic equivalence between the two types of reaction. Thus, ring enlargement has been found to be more robust in the face of incorporation of a B sub-group metal as an alloying component in Pt or Rh than is a simple alkane bond-shift reaction, at least when evaporated metal film catalysts are used.[6,7] The distinction is most marked with reactants having a quaternary carbon centre and a dimethylcyclopentadiene intermediate having non-classical bonding to a surface metal atom was suggested for ring enlargement of 1,1-dimethylcyclopentane on Pt and Pt–Au.[6]

The reaction of 1,1,3,3-tetramethylcyclobutane (TMCB) on platinum and other metallic surfaces offers the opportunity of extending the available information. This choice was encouraged by an aim, not completely realised, of probing the degree of dehydrogenation of the ring-enlargement intermediate on Pd and Pt using deuterium as a tracer as previously reviewed.[3] Reactions are reported on these and a number of other

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metallic elements located throughout the transition-metal block prepared as evaporated films. Discussion of the ring-opening reaction to 2,2,4-trimethylpentane (TMP) is also of interest mechanistically because neither the selective nor the non-selective route of ring opening (SCM, NSCM, in the terminology of Gault[5]) is available to TMCB for reasons which have been detailed.[3] It has previously been shown that in the equally strained reactant 1,1-dimethylcyclobutane the endocyclic C—C bonds adjacent to the quaternary substituents do not undergo scission on platinum films at 573 K.[8] This has long been the experience with larger rings.[9]

Experimental

A static reaction system made from Pyrex glass was used both for an initial study of the homogeneous (uncatalysed) thermal decomposition of TMCB and for the catalytic experiments. Single metal or alloy films were prepared by evaporation from appropriate metal filaments as previously described.[3] Metals were of best research grade and deuterium/hydrogen was palladium-diffused.

The TMCB was synthesised by Wolff–Kischner reduction[10] of 1,1,3,3-tetramethylcyclobutane-2,4-dione. The major impurity following fractionation was 3–4% of 2,2-dimethylpentane, and this material was used directly.

Ta, Ti, Zr and Mo films were examined for catalytic activity directly after deposition at 273 K ('unsintered'). Pt, Pd, Rh and Ir films laid with the vessel wall at 773 K were then heated in hydrogen or deuterium at the same temperature for 2 h before admitting the reaction mixture ('sintered'). The standard reaction mixture contained 1:10 hydrocarbon to hydrogen (or deuterium) partial pressures, with 0.6 Torr† TMCB in the 600 cm^3 reaction vessel.

Analysis of hydrocarbon mixtures was effected during reaction by g.l.c. sampling (column of OV1 on Chromosorb P at 303 K) and by *in situ* mass spectrometry (by Kratos MS10c2). Deuterium contours of reaction products was determined by later g.l.c.–m.s. analysis of vessel contents on a separate instrument, as previously detailed.[3] A number of confirmatory analyses of products of the TMCB–hydrogen reaction were also carried out by the same means. Product distributions to be presented cannot distinguish between isobutane and isobutene; for the homogeneous reaction, however, literature reports make it clear that the iC_4 product here is isobutene.

All results to be presented are for initial reactions because conversions were kept below 5% (except for Ta at higher temperature).

Results

The Homogeneous Reaction

Results of blank-run experiments on the gas-phase decomposition of TMCB in excess hydrogen (table 1) show the major product to be isobutene with a smaller proportion of lighter hydrocarbons at the lower temperatures and minor production of 1,1,3-trimethylcyclopentane (TMCP) at higher temperatures. This homogeneous decomposition commenced at 600 K or a little higher. The activation energy derived for the production of isobutene of 240 kJ mol^{-1} agrees satisfactorily with published values of 273 kJ mol^{-1}[11] and 270 kJ mol^{-1}.[12]

Workers have favoured a biradical mechanism for the uncatalysed reaction as rationalised by Woodward and Hoffmann.[13] Expected products from the biradical intermediate are isobutene, 2,4,4-trimethylpent-1-ene and TMCP of which the former dominates and the second has been observed.[12]

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† Torr = 101 325/760 Pa.

Table 1. 'Blank' (uncatalysed) reaction and initial product distributions of TMCB/hydrogen on unsintered films of early transition metals (TMCB/H_2 ratio of 1/10)

catalyst metal	T/K	C_1–C_3	iC_4	TMP	TMCP	k/% min^{-1}[a]
no catalyst	623	35	65	—	—	0.003
	658	18	82	—	—	0.008
	685	5	93	—	2	0.039
	715	1	97	—	2	0.374
Ti	693	—	99	—	1	0.23
Zr	585	—	100	—	—	0.011
	647	—	100	tr	—	0.014
	697	6	92	tr	2	0.52
Mo	465	—	tr	100	—	0.88
	498	24	76	—	—	0.07
	542	—	91	9	—	0.40
Ta[b]	487	—	81	19	0.3	0.90
	516	—	100	—	—	0.62

[a] Per 10 mg metal in the runs with metal catalysts. [b] With tantalum traces of partially demethylated TMCB species were observed.

Catalysis by Early Transition Metals

Unsintered Ti and Zr films are not considered to catalyse the reactions of TMCB at all because rates of reaction and product distributions are indistinguishable from those of the homogeneous reaction (table 1). Although self-poisoning was a marked feature (as it was to a lesser extent in all the catalytic runs), the reaction of TMCB on Mo was clearly metal catalysed, the products being those of ring-opening and hydrogenolysis. Hydrogenolysis was the dominant feature of the tantalum-catalysed reaction.

Catalysis by Platinum Metals

Representative results are given in table 2. In these experiments which were designed primarily to suggest suitable reaction temperatures and times for deuterium runs (*vide infra*), C_1–C_3 products were not resolved from iC_4 in the g.l.c. except in the case of early transition metals and Pt–Cu alloy films where a different column condition was used.

The dominant process on rhodium films was extensive hydrogenolysis with a trace of ring enlargement. The latter feature was somewhat irreproducible from run to run. Extensive hydrogenolysis was found on iridium at all reaction temperatures; a run at a lower hydrogen/TMCB ratio (2.7:1), prompted by a study of methylcyclopentane reactions,[14] did not reveal any TMCP or TMP product.

On palladium, ring scission to TMP was by far the major process, with further break-up to C_1–C_4 a lesser reaction and ring enlargement to TMCP a still more minor route. With platinum selectivity for ring opening to TMP and for ring enlargement to TMCP are comparable and together dominate the reaction. Two Pt–Cu alloy films, prepared as previously described[3] and having widely different Pt/Cu ratios, gave ring enlargement as a major fraction of the reaction, even at 4 atom % Pt. Simple ring scission to TMP was relatively reduced (to *ca.* 25 % ring enlargement) on both alloy films. However, there is further break-down to lighter hydrocarbons, particularly on the high-copper film, but the temperature required for reaction is now $\geqslant$ 550 K.

Table 2. Initial product distributions of TMCB/hydrogen on sintered platinum-metal films ($TMCB/H_2$ ratio of 1/10)

catalyst metal	T/K	C_1–C_4	[a]	TMP	TMCP	k/% min^{-1} (10 mg $metal)^{-1}$
Rh	542	96	$2._5$	—	$1._2$	0.15
	625	100	—	—	—	0.91
Ir	462	100	—	—	—	0.03
	495	100	—	—	—	0.04
	523	100	—	—	—	0.08
	567	100	—	—	—	0.27
Pd	475	24	$0._3$	73	3	0.04
	534	12	11	68	9	0.05
Pt	447	35	—	46	19	0.08
	472	8	—	47	45	0.19
	502	11	—	44	45	0.21
88 Pt–12 Cu	457	—, *ca.* 80[b]	—	—	*ca.* 20	0.003
	533	—, 15	—	15	70	0.03_3
4 Pt–96 Cu	555	62, —	—	[c]	38	0.003
	584	47, —	—	11	42	0.002

[a] Partially demethylated TMCB (see table 1). [b] Respective production of C_1–C_3 products and of iC_4 which were resolved in the g.l.c. conditions used for Pt–Cu experiments. [c] Small, not measurable due to analysis limitations.

Deuterium Study

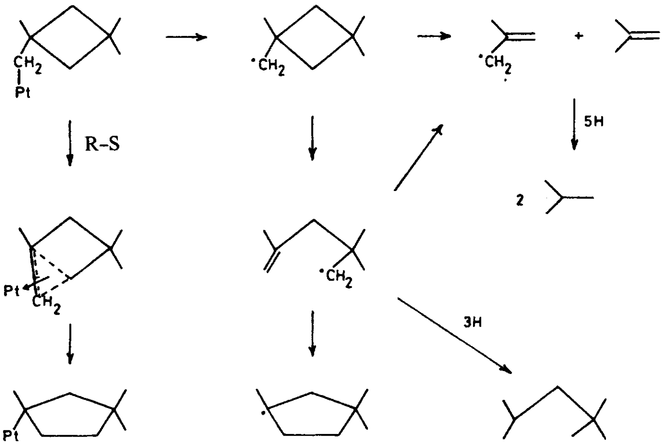
The final part of this work was the g.l.c./m.s. analysis of TMCB/deuterium reaction products on sintered films of those noble metals (Pt and Pd) which were active for non-destructive processes.

A wide range of catalyst pretreatments failed to produce a metal surface on which deuterium exchange in the products TMCP and TMP had not proceeded too rapidly to permit observation of the lowest possible deuterium content (which would correspond to deuterogenation of the surface intermediate). Such pretreatments included extended sintering, varying the reaction time and temperature and predosing with carbon monoxide. The lowest deuteroisomers observed for Pd were $[^2H_4]$TMP and $[^2H_4]$-TMCP: the shape of the deuterium-containing product contours and some lack of reproducibility of the cut-off point around $^2H_4$ give rise to doubt as to whether the lowest deuterium content in the two products had been observed.

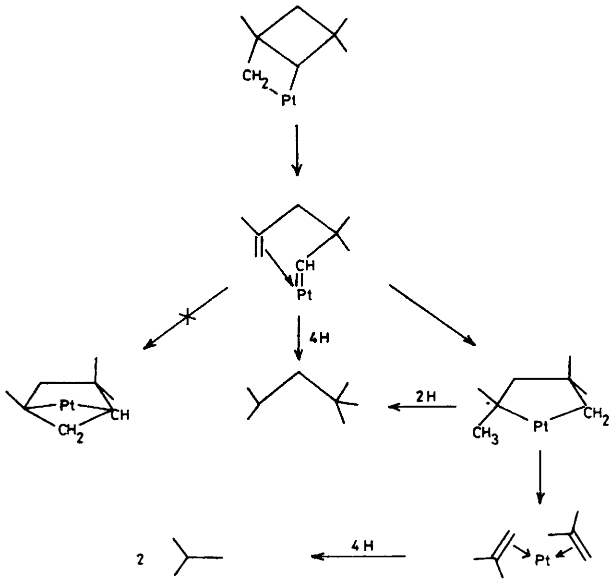
Discussion

Earlier reviews[15,16] have developed the speculation that a metal atom having *d*-orbitals of appropriate symmetry may offer a catalytic pathway to reaction of cyclobutane. The bulky geminal dimethyl groups of TMCB clearly prevent such interaction with a metal centre, as can be demonstrated by a molecular model. Such mechanisms, without the need to pass judgement on their validity, may thus be excluded from further consideration in the discussion of TMCB reactions.

The similarity of reaction products on Ta and Mo to those in the homogeneous reaction of TMCB which takes place at higher temperatures might suggest that the catalysis occurs by a free-radical reaction mediated by the metal. Reaction schemes may be constructed, related to those proposed in the literature for the homogeneous decomposition[11,12] and also considered for reactions of metal complexes,[17] which



Scheme 1. Free-radical reactions mediated by metal. The Rooney–Samman route (R–S), referred to in the discussion, is also shown.



Scheme 2.

rationalise the production of isobutene, 2,4,4-Trimethylpent-1-ene and of TMCP (scheme 1). Such a mechanism cannot at present be totally excluded, and in its favour is the rather specific production of isobutene (isobutane) in the catalysis. The preference must lie, however, with mechanistic proposals based on surface-bound radicals which have general validity for ring opening and ring enlargement of cyclic alkanes and bond shift of acyclic alkanes. We note that a free-radical-type mechanism which rationalises the hydrogenolysis and isomerisation of neopentane is difficult to devise. Hydrogenolysis and ring enlargement will now be considered in turn in relation to catalytic mechanisms already argued in the literature.

The persistent formation of isobutene (isobutane) in the TMCB reaction originates, we believe, in the symmetrical scission of a metallocyclopentane intermediate (scheme 2) which is now well documented in organometallic reactions.[6, 18] Thus, the $\alpha\gamma$ adsorbed species formed initially leads through a carbene–alkene intermediate either (i) to TMP by total hydrogenation or (ii) by limited addition of hydrogen atoms to give the metallocyclopentane shown which cracks symmetrically, yielding two isobutene fragments. Looking ahead to the following discussion, we note that bond-shift is not possible by the metathesis-type mechanism[5, 19] for this structure, that is by direct 1,5-cyclisation of the carbene–alkene intermediate mentioned. This would be impossible sterically (scheme 2).

The ring enlargement of TMCB to TMCP is entirely analogous to that of the adamantene dimer which has geminal substitution at C-1 and C-3 of a cyclobutane ring. This reaction takes place rapidly at 483 K on platinum catalysts and similarly on palladium.[20] Some observations and assessments will now be made on available information on bond shift and ring enlargement followed by comments on the present reactant.

The supposed uniqueness of platinum as a catalyst metal for bond shift of quaternary carbon centres has been shown in recent years to be untrue. At the same time the difference in reactivity in the bond-shift reaction of non-quaternary and quaternary carbon centres has been shown not to represent a fundamental difference in kind. Thus palladium has been shown to be initially active for neopentane rearrangement but shows rapid self-poisoning due to carburisation.[21] A rhodium–tin evaporated alloy film was active in homologation of neopentane to benzene at 600 K, implying bond-shift rearrangement of the reactant in an initial step.[22a] Muller and Gault[23] reported 1,1,3-trimethylcyclopentane ring enlargement at the quaternary centre to give xylenes as 88 % of aromatics production at 573 K on platinum and as 10–20 % of aromatics produced on palladium, rhodium and iron at a similar temperature. An early report of neopentane isomerisation on iridium[24] was questioned.[25] Subsequently, sintered iridium films were reported to produce xylenes from 1,1,3-trimethylcyclopentane, but only above *ca.* 630 K, and a meaningful xylene/toluene ratio could not be observed because of cracking.[22b] In a later, comprehensive study, the neopentyl-group bond shift of 2,2,4,4-tetramethylpentane was found to be measurable below 470 K on each of the platinum metals.[3] Metals other than Pt have, then, non-negligible activity in isomerisations at quaternary centres and further there is no good reason to make a distinction in kind between the bond shift of alkanes and ring-enlargement processes. The usually more rapid ring enlargement achieves relief of ring strain and consequently has a greater driving force. Bond shift at a quaternary centre appears from general experience to be retarded by carburisation and to be more prone to self-poisoning.

The similar persistence of TMCB ring enlargement on a Pt–Cu alloy of high percentage Cu to the 1,1-dimethylcyclopentane ring enlargement on Pt–Au at high percentage Au shows that the dimethylcyclopentadiene-type intermediate postulated for the latter[6] is unnecessary. No analogous structure is possible for TMCB. The Rooney–Samman mechanism[1] (scheme 1, 'R–S') rationalises both reactions.

Finally, a comment is offered on the product distributions for the Pt–Cu alloy films. The trend toward deeper cracking within the hydrogenolysis route when platinum is extremely diluted by copper (4 Pt–96 Cu film of table 2) is in harmony with previous studies of Pt–Cu alloy catalysts. Ponec and co-workers have reported that similar dilution of iridium, palladium, nickel or platinum with copper leads to catalysts having increased activity for hydrogenolysis: this is in contrast to the effect of dilution with gold, silver or tin.[26, 27] In particular, a greater proportion of methane in the hydrogenolysis products with Pt–Cu is found.[28] We believe that the copper acts by furnishing a matrix in which a very high dispersion of platinum is promoted and maintained. Analogous behaviour of phosphorus in platinum catalysts derived from 'Chatt' clusters and which showed very selective demethylation activity has been indicated previously.[29] Mechanistically, the sites giving rise to $\alpha\gamma$ adsorption have in the present study at 4 Pt–96 Cu been sufficiently modified to lead to other forms of multiple bonding than those depicted in scheme 2. The platinum has, in effect, assumed nickel-type behaviour.

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