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The Mechanism of Conversion of Saturated Hydrocarbons Catalyzed by Sulfated Metal Oxides: Reaction of Adamantane on Sulfated Zirconia[1]

Dan Fărcaşiu,[2] Anca Ghenciu, and Jing Qi Li

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, Pennsylvania 15261

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The high activity of sulfated zirconia (SZ) toward hydrocarbon conversions has been confirmed by the study of the isomerization of methylcyclopentane to cyclohexane. This catalytic activity is generally rationalized by the catalyst having superacidic strength. The reaction of methylcyclopentane with superacids is initiated, however, by the cleavage of a carbon–carbon bond with the formation of an acyclic carbocation, followed by hydride transfer giving the methylcyclopentyl cation which undergoes rearrangement. By contrast, no isohexanes (products of ring cleavage) were formed in the reaction on SZ, suggesting a different reaction mechanism. The mechanism of interaction of SZ with saturated hydrocarbons was elucidated by a study of adamantane. Small amounts of 1-adamantanol and adamantanone and traces of 2-adamantanol were observed after reaction at temperatures from 65 to 135°C, indicating that the reaction is an oxidation followed by hydride transfers. Small amounts of diadamantanes were also formed, proving that oxidation to carbocations goes through the free radical stage. At 150°C, additional reaction products were observed, 1-adamantanethiol (larger amount) and 2-adamantanethiol (smaller amount), indicating reduction of sulfate all the way to sulfide, which then traps the adamantyl cation in competition with the oxygen anions or water formed in the redox process. Ring cleavage and disproportionation to form alkyladamantanes and aromatics also occurred. Thus, the increase in activity of SZ over the parent oxide for carbocationic alkane and cycloalkane reactions can be ascribed to initiation through a one-electron oxidation of the hydrocarbon by sulfate to a carbocation precursor. © 1996 Academic Press, Inc.

INTRODUCTION

In 1976 it was reported that catalytic properties of acidic metal oxides can be enhanced by incorporation of small amounts of sulfate anions (1). These materials have shown high activity as catalysts for carbocationic reactions (1, 2). As it was shown that the surface of the activated oxides is modified by sulfate ions (3), the significantly higher activity over that of the untreated metal oxide can be assigned to the presence of sulfur(VI) species.

Even though a significant increase in catalytic properties was observed for metal sulfates upon calcination (4), the sulfated metal oxides (SMO) are not described as surface metal sulfates. Instead, it was concluded from XPS spectra that the surface of sulfated zirconia (SZ) consists of ZrO_2 and "SO_4," rather than $Zr(SO_4)_2$ (5). The sulfate groups are generally considered to be covalently bonded to the metal oxide lattice, but there seems to be no satisfactory description of the structure of the surface species (2e, 3b–3d). According to one model, each sulfur atom is connected to the lattice through two tricoordinated oxygen atoms, a rather peculiar bonding scheme (3b, 3c, 3e). According to another, the sulfur is bonded to three metal atoms by S–O–*M* bonds and Brønsted acidity is generated by cleavage of one of these bonds by water and formation of an $(M\text{–}O)_2S(=O)\text{–}OH$ group (6), which implies an unusual oxidation level of sulfur, S(V). It was also indicated that as the sulfur loading increases, structures with S–O–S bonds, similar to pyrosulfuric or higher polysulfuric acids, may exist on the surface (6b, 7). According to other authors, very strong acid sites and basic sites coexist in the vicinity of each other, such that in some reactions a high selectivity is achieved by the mechanism of

$$\begin{aligned} AH + S + {:}B &\rightarrow A^- + S{-}H^+ + {:}B \\ &\rightarrow A^- + P + B{-}H^+, \end{aligned} \qquad [1]$$

where S and P are the substrate and product, respectively (8). What was not noticed, however, is that for the process to proceed as written, B: has to be a stronger base than A^-; therefore the process stops after one molecule of S is converted, instead of being catalytic. For catalytic activity it is required that AH and BH^+ be of about the same

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[2] To whom correspondence should be addressed.

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strength. In general, even if basic sites can be generated together with the acid sites in the preparation of the catalyst, as soon as the latter interacts with the first molecules of substrate, no basic sites stronger than the conjugate base of the acid sites can exist on the surface.

It has been rather generally considered that SMOs are superacids, with respect to both their Brønsted and their Lewis sites (2, 3, 9). This property should then explain their catalytic activity. Based on IR studies of adsorbed pyridine it was concluded that sulfate deposition converts Lewis acid sites to Brønsted sites and maximum activity is achieved at an intermediate level of sulfation (ca. 150 μg S/m^2) where the Brønsted and Lewis sites are about equal in number (10). The very same type of measurements, however, led other authors to the conclusion that there are almost no Brønsted sites on SZ; such sites are generated, particularly in samples calcined at lower temperature, when water is adsorbed by the solid (7b, 11). Still other researchers found that the sulfur content has no effect on conversion in cracking and isomerization (12).

It was reported that sulfation retards crystallization of metal oxides (13), but it was not indicated how this bulk structural property is connected with the superacidic strength of surface groups or how the structure of the sulfated surface is influenced by it.

This paper will examine whether superacidity is the reason for the catalytic activity of SMOs and will probe the actual mechanism of activation of saturated hydrocarbons on these catalysts.

EXPERIMENTAL

General. The reactants and solvents used were AR commercial materials and were used as purchased. The catalyst surface area and sulfur content were measured as described before (14).

GLC analyses of MCP isomerization experiments were run on a Hewlett–Packard 5890 Series II instrument, on a 3 m × 3 mm OD column packed with 10% methyl silicone SP2100 on 60/80 mesh supelcoport, held at 30°C for 8 min, then heated to 120°C at a rate of 10°C/min.

The GC–MS analyses were conducted on a HP 5890 Series II gas chromatograph/HP 5970 Series MSD, on a 50 m × 0.2 mm capillary column, coated with HP1 crosslinked silicone (0.33 μm), held at 150°C for 10 min, then heated to 280°C at a rate of 15°C/min and kept at 280°C for 40 min. The MS was acquired in the EI mode, at 70 eV.

Catalyst preparation. SZ was prepared from $Zr(OH)_4$ or from ZrO_2, by the controlled impregnation technique (14). Precipitation of $Zr(OH)_4$ was conducted by mixing $ZrO(NO_3)_2$ and NH_4OH in water at pH 7 ± 0.5 (15). The solid was filtered, washed, and dried at 150°C overnight. Calcination at 500°C for 4 h gave ZrO_2.

For sulfation, the precursor, $Zr(OH)_4$ or ZrO_2, was ground in a mortar, then covered with the amount of 1 *N* H_2SO_4 shown in Table 1 and kept at room temperature for 2 h. Solvent evaporation and drying (one step) were conducted by heating in an oven at 150°C overnight. The solid was then calcined at 600 or 550°C, as shown in Table 1.

The catalyst was prepared in 10-g batches. Each batch was characterized by sulfur analysis, BET surface area (Table 1), and activity toward isomerization of MCP (Fig. 1).

Isomerization of MCP (14). The catalyst (0.09–0.12 g) was introduced into a 12 cm × 5-mm i.d. glass tube and activated at 450°C for 2 h. The tube was capped with a rubber septum and allowed to cool to room temperature. The reactant (4 ml per gram of catalyst) was injected with a syringe and the tube was placed in an oil bath at 65°C. At the beginning of the experiment the vials were manually shaken for the liquid to penetrate the catalyst. Samples were withdrawn at intervals with a syringe and analyzed by GLC to check the products and conversions. Two such tubes were run for each catalyst sample; the agreement was very good. The catalytic activities of various batches of catalyst are presented in Fig. 1.

Adamantane conversion. The reaction was run in glass tubes as discussed above, and the catalyst was activated in the same way (450°C, 2 h). When the tubes reached room temperature, the caps were removed and adamantane (AdH) (small crystals) was added quickly through a funnel. The tubes were recapped immediately and sealed in flame. After being sealed and cooled, each tube was shaken to mix the contents, then immersed completely in an oil bath at room temperature. The temperature was increased to the desired value in 30–90 min and held there for 2–16 days, as shown in Table 2. During the reaction the tubes were occasionally rolled over in the oil bath. At the end of the reaction, each tube was cooled to room temperature, cut open, and its contents were poured into acetone or benzene. The mixture was boiled and stirred for several minutes, then filtered with suction and the solid was extracted once more on the filter. The extraction with acetone is more efficient, but small amounts of mesityl oxide and diacetonealcohol are formed because the catalyst is still active. These impurities elute quickly from the GLC column and do not affect the analysis of the reaction products. To avoid further reactions of the solvents used for extraction with the catalyst, for some experiments the reaction mixture was first quenched in water (ca. 1 hr on standing) and then the organic products were extracted in the chosen solvent. For these experiments, ethyl ether was a better solvent. The composition of products, determined by GC–MS, was the same for either extraction solvent and is shown in Table 2. The numbers given represent relative amounts; in all cases adamantane was by far the major component. This feature complicated the analyses because in order to

TABLE 1

Characterization of Sulfated Zirconia Catalysts

No.	Catalyst	Starting material	ml 1 *N* H_2SO_4/g cat	Calcination temp., °C^a	Surface area, m^2/g^b	Sulfur analysis, %^{c}	Specific rate^d × 10^2 mmol/h · m^2
1	SZCH-0.95-1^e	$Zr(OH)_4$	0.95	600	101.4	1.56 (0.03)	1.08
2	SZCH-0.95-2^e	$Zr(OH)_4$	0.95	600	105.1	1.56 (0.005)	1.58
3	SZCH-0.95-3^e	$Zr(OH)_4$	0.95	600	106.7	1.57 (0.018)	1.82
4	SZCH-0.95-4^e	$Zr(OH)_4$	0.95	600	101.7	1.50 (0.012)	1.91
5	SZCH-0.95-5^e	$Zr(OH)_4$	0.95	600	105.9^f	1.70 (0.004)	1.07
6	SZCO-0.95^g	ZrO_2	0.95	550	46.8	0.94 (0.013)	0.271
7	SZCO-2.00^g	ZrO_2	2.00	550	56.7	1.55 (0.014)	0.278

[a] Entries 1–5 have been calcined for 5 h, whereas entries 6 and 7 have been calcined for 4 h, at the indicated temperature.

[b] BET measurements, as described in Ref. (14).

[c] Sulfur analysis (average of three determinations, standard deviation in parentheses).

[d] Initial rates calculated from the pseudo-first-order rate constants, determined from the conversions up to 4.7 h for SZCH and 9 h for SZCO, uncorrected for catalyst deactivation, for a ratio substrate/catalyst of 4/1 (w/w) and normalized with respect to the specific surface area.

[e] Sulfated zirconia controlled impregnation technique, from zirconium hydroxide, 0.95 ml 1 *N* H_2SO_4 per gram of $Zr(OH)_4$; various batches are indicated by numbers 1–5.

[f] Average of two measurements (±0.6 m^2).

[g] Sulfated zirconia controlled impregnation technique, from zirconium oxide, 0.95 and 2.00 ml 1 *N* H_2SO_4 per gram ZrO_2, for entries 6 and 7, respectively.

analyze the minor components, the solution had to be concentrated until AdH started to crystallize out; cocrystallization of small amounts of the compounds of interest is possible. Therefore, the quantitative analysis is only approximate. In most cases, duplicate or triplicate experiments were run; good reproducibility was observed.

The mass spectra of compounds identified (from standards available or from literature data (16–18)) are listed in the Appendix in the order of elution (peak intensities given as percent from the base peak). The sulfur-containing compounds were identified by subjecting the mixture from the reaction on SZCO-2.00 to GLC analysis with a sulfur ionization detector (SID).

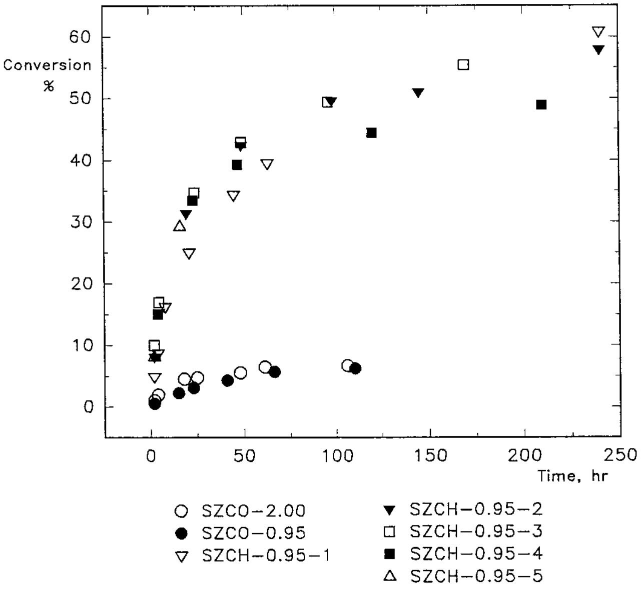


FIG. 1. Isomerization of MCP on SZ catalysts.

Conversion of a mixture of adamantane and adamantanone. The general procedure for conversion of AdH (above) was used. After the activation of catalyst (450°C, 2 h) and cooling of the reaction vial to room temperature, a mixture of AdH and Ad=O (molar ratios: AdH : Ad=O = 9.68 : 1, S/AdH = 1.0) was quickly introduced through a funnel and the tube sealed in flame. Thus, there was an excess of substrate over sulfate in this experiment. The tube was heated for 68 h at 135°C, then for 4 h at 150°C (total time 72 h). After the reaction, the mixture was quenched in water and extracted in diethyl ether. No adamantanone was present in the reaction mixture.

1,1′-Diadamantane synthesis. Attempts to synthesize 1,1′-diadamantane from 1-bromoadamantane and sodium in xylene by a procedure described in the literature (18) gave no desired product. Instead, adamantane, dixylyl isomers, and at least three isomeric adamantylxylenes were formed. Another synthesis of diadamantane, from 1-bromoadamantane and magnesium in diethyl ether (19a), gave very poor yields. We performed, therefore, a Wurtz reaction in *n*-heptane. Sodium (1.2 g, 5% excess) freshly cut under heptane was quickly introduced in a 100-ml three-necked flask containing 50 ml of heptane and a magnetic stirrer, under nitrogen. After heating to boiling under reflux, a solution of 10.7 g 1-bromoadamantane in 35 ml

TABLE 2

Relative Amounts of Selected Products in the Reaction of Adamantane over Sulfated Zirconia[a]

Catalyst	Reaction conditions	S/AdH molar ratio	Products and quantities[b]				
			$Ad{-}CH_3$	1-AdOH	$Ad{=}O$	Ad−Ad	S compounds[c]
SZCH-0.95-3	65°C, 216 h	0.93	1	18	23	6.7	—
SZCH-0.95-1	90°C, 432 h	1.51	1	2.3	5.4	Traces	—
SZCH-0.95-1	90°C, 216 h	1.51	1	1.35	5.2	Traces	—
SZCH-0.95-2	120°C, 48 h	1.40	1	0.6	4.4	6.8	—
SZCH-0.95-4	135°C, 48 h	0.98	1	0.1	0.1	Traces	—
SZCH-0.95-4	135°C, 48 h	1.36	1	0.55	0.2	0.44	—
SZCH-0.95-2	150°C, 48 h	0.91	1	Traces	—	Traces	0.08
SZCH-0.95-5	150°C, 72 h	1.59	1	—	—	Traces	—
SZCH-0.95-3[d]	150°C, 48 h	1.00	1	1	9.9	—	7.3
SZCO-0.95	150°C, 168 h	1.38	1	—	12.61	0.15	4.8
SZCO-2.00	150°C, 72 h	3.15	1	0.25	0.70	—	1.1

[a] With the exception of $Ad{-}CH_3$ and Ad–Ad, alkyladamantanes and other products resulting from coupling reactions are not listed.

[b] Relative GC peaks areas.

[c] Ad–SH, Ad–S–Ad, Ad–S–S–Ad (all isomers).

[d] Catalyst exposed to air before reaction.

heptane was added from a dropping funnel for 2 hr at the same temperature, with stirring. Boiling and stirring under nitrogen continued for 24 h. The reaction mixture was filtered while hot and the precipitate was washed with hot heptane. 1,1′-Diadamantane (1,1′-Ad–Ad, 2.03 g) crystallized from the combined filtrate (97% purity, 3% AdH as impurity, by GC–MS analysis). The mother liquor was concentrated to ca. 20 ml and analyzed by GC–MS. It contained (as solutes) 10.1% AdH, 37.4% heptyladamantane isomers, and 52.5% 1,1′-diadamantane. Upon cooling to room temperature, 0.96 g of 1,1′-diadamantane precipitated (overall yield 1,1′-diadamantane, 45%). Recrystallization from benzene gave mp = 280–285°C (literature: 288–290°C (18) or 296°C (20a)).

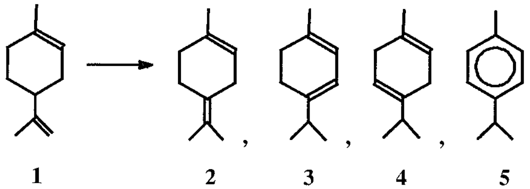
RESULTS AND DISCUSSION

Attempted Correlation of Catalytic Activity with Acidity Measured by H_0

The claim of superacidity of SMOs was based on H_0 parameters deduced (2–5) from the examination of color changes of Hammett indicators adsorbed on the solids (21) and on catalytic activity. Some bothersome inconsistencies exist, however, in the results published on the subject. Table 3 presents data on H_0 parameters and catalytic activity in some hydrocarbon conversion reactions. (The idea that reactions such as esterification of alcohols with carboxylic acids should correlate with superacidity (3e, 9a) cannot be entertained seriously.) The reported acid strengths do not explain why sulfated Fe_2O_3 (SFe) is more active than sulfated titania (STi) for isomerization of butane. It is also hard to understand why deposition of platinum on SZ (Pt/SZ) significantly decreases the acid strength but has little effect on butane isomerizing ability. Indeed, based on the published H_0 values, Pt/SZ should be less active for this reaction than STi, whereas silica–alumina (Si–Al) should be about as good as Pt/SZ. Also, there is no report that sulfated alumina (SAl) isomerizes butane at room temperature; if "superacidity" measured by H_0 was the reason for activity, one would expect it to be at least as good as SFe.

The second reaction listed in Table 3, isomerization of cyclopropane to propene, has been repeatedly offered as a test of superacidity of SMOs (3, 9b 22). Again, a comparison of SSn, STi, and SAl shows that there is no connection between H_0 values and catalytic activity. As the two results for SFe show, the method of preparation of the metal oxide has a much more pronounced effect on the activity than the differences in H_0. Considering, however, that acid cleavage of cyclopropane occurs smoothly at 25°C in 57% H_2SO_4 (23) (H_0, −4.15) (24, p. 26) and in trifluoroacetic acid (25) (H_0, −3.0) (24, p. 216)), it looks most likely that all rate differences for this reaction in Table 3 are due to reasons other than differences in acid strength.

The last example chosen in Table 3 is the isomerization of limonene (**1**) to terpinolene (**2**), α-terpinene (**3**), and γ-terpinene (**4**), accompanied by a small amount of dehydrogenation to p-cymene (**5**) (8a):



1 **2** **3** **4** **5**

[2]

TABLE 3

Reported Acidities and Catalytic Activities of Sulfated Metal Oxides

			Catalytic activity for isomerization of hydrocarbons				
			Butane (BuH)^{b}				
No.	Catalyst^{a}	H_0	A	B	C	Cyclopropane^{c}	Limonene^{d}
1	SZ	$<-16.04^{e}$	$20.4^{e,f}$ $31.6^{e,g}$		49	243	20.4
2	SSn	$<-16.04^{h}$	$8.4^{h,i}$	$28.6^{h,j}$		49	^{k}
3	STi	$-16.04 < H_0 < -14.52^{l}$		$4^{l,m}$		226	^{k}
4	SFe	$-16.04 < H_0 < -12.7^{n}$		18^{o}		202 815^{p}	0
5	SA1	$-16.04 < H_0 < -14.52^{q}$	^{k}			69	^{k}
6	Pt/SZ	-12.7^{r}			43	^{s}	^{k}
7	Si–Al	$-12.70 < H_0 < -11.35^{t}$ $-13.75 < H_0 < -13.16^{u}$	0^{v}				87.7

[a] SSn: SO_4/SnO_2; STi: SO_4/TiO_2; SFe: SO_4/Fe_2O_3; SA1:SO_4/Al_2O_3; Pt/SZ: $SO_4/Pt/ZrO_2$; Si–Al silica–alumina.

[b] Reaction at 25°C, in a recirculation reactor; conversion (%) after 24 hr. A: 0.3 g of catalyst per 7.8 ml (NTP) BuH, B: 1 g of catalyst per 7.8 ml (NTP) BuH, C: Reaction in a flow reactor, in He, at (presumably) 250°C; initial conversion (Ref. 21).

[c] Rate in μmol/(min · g) at 100°C, in a recirculation reactor; all data from Ref. (3c), unless stated otherwise.

[d] Conversion (%) at 30°C after 1 h, in a batch reactor (Ref. 8).

[e] Ref. (2e); In ref. (2c) a value of $-16.04 < H_0 < -14.52$ is given.

[f] Catalyst activated at 500°C in air for 1.5 h before reaction; 15 ml (NTP) BuH, 0.7% disproportionation.

[g] Catalyst activated at 250°C and 10^{-3} mm Hg for 3 h before reaction; 15 ml (NTP) BuH, 1.1% disproportionation.

[h] Ref. (2k).

[i] Reaction at 30°C, 1.0% disproportionation.

[j] Reaction at 30°C, for 20 h; 3.2% disproportionation.

[k] Not studied.

[l] Ref. (2d).

[m] Only traces of disproportionation products were seen.

[n] The indicator color change cannot be seen on this material. It was determined indirectly that it is weaker than SZ and stronger than Si–Al (Ref. 2b, 8).

[o] The extent of disproportionation was not reported (Ref. 2b).

[p] $Fe(OH)_3$ used for catalyst preparation was precipitated from alum with urea (Ref. 3a).

[q] Ref. (2j).

[r] Ref. (3e).

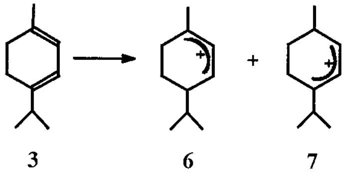
[s] Ca. 50% conversion in 5 min and ca. 85% in 45 min, but no rates were measured (Ref. 22b).

[t] Ref. (2b).

[u] Ref. (9b).

[v] Ref. (8).

Among the three catalysts investigated, Si–Al is the most active and SFe is inert. SZ, albeit four times less active than Si–Al, was preferred for this reaction on account of its higher selectivity to the desired product, **2** (8a). The selectivity represents kinetic, rather than thermodynamic control, because **3**, with endocyclic and conjugated double bonds, is the more stable isomer. Thus, the high selectivity indicates that the carbocations formed by hydronation of **1** and **2**, even though tertiary, do not intervene as intermediates with kinetically significant lifetimes in the reaction on SZ. Instead, cationoidic species (“weakly coordinated carbocations”) (26) are involved. The reaction stops at **2** because its tetrasubstituted double bond is sterically hindered to further reaction. If SZ possessed very strong acid sites, the allyl cations **6** and **7** should be formed by hydronation followed by hydride shifts:


3 **6** **7**

[3]

If we could speak of "superacidity" of the surface sites, we would expect the well-established ring contraction to occur, leading to cyclopentenyl cations, species characterized by very high stability and low acidity (27), which should poison the catalyst. It was established that even the parent cyclohexenyl cation undergoes ring contraction with a half-life of less than 4 h at 0°C (28) and that the alkyl-substituted ions like **6** and **7** react significantly faster (27, 29).

It can be argued that the differences observed in catalytic activity arise from a combination of differences in acid strength and differences in surface area. An evaluation of this possibility is difficult to make in most cases, because surface areas of SMOs are seldom reported. Nonetheless, it can be observed that the similar activity of SZ and Pt/SZ, the former being more than 2000 times stronger an acid, would require a similar ratio in specific surface area favoring the latter! In fact, considering that preformed SZ was impregnated and recalcined to form Pt/SZ, one cannot argue that Pt/SZ had a surface area greater than SZ even by a much smaller factor in the experiments comparing the two materials (21). In another case, SZ and SSn were reported to differ in surface area by ca. 20% (22a), much less than the activity differences obtained by the same authors for the isomerization of butane (Table 3). Thus, differences in surface areas cannot be invoked to explain the discrepancies between H_0 values and catalytic activities.

From the examination of the literature on the subject, it appears that the terms "superacid" and "superacidity" have been used rather loosely to characterize various solid materials with catalytic activity. Thus, even a catalyst obtained by exposing silica gel to SO_2Cl_2 and calcining in air at 400°C was referred to as a superacid because it was active for dehydration of ethanol (9a). Some misunderstandings can be found even of actual strengths and ranking of superacids in solution. For example, the 7 : 1 HF–SbF_5 mixture has been listed as similar in strength to fluorosulfonic acid, 30 times weaker than 20 : 1 FSO_3H-AsF_5, and more than 6000 times weaker than 9 : 1 FSO_3H-SbF_5 (9b, 30), at variance with the relative hydronation abilities determined both from kinetic (31) and equilibrium measurements (32).

The poor correlating ability of H_0 values for properties of solid acids is not surprising; in addition to the operational drawback of measuring a color change of the indicator, rather than the position of a hydronation equilibrium, there is a theoretical objection to the approach, which becomes apparent when one considers the definition of the acidity function by Hammett

$$H_0 = (\mathrm{p}K_{\mathrm{BH}^+}) - \log\frac{[\mathrm{BH}^+]}{[\mathrm{B}]} \qquad [4]$$

and its equivalent (33, 34):

$$H_0 = -(\log a_{\mathrm{H}^+}) + \log\frac{\gamma_{\mathrm{BH}^+}}{\gamma_{\mathrm{B}}}. \qquad [5]$$

It was emphasized that H_0 measures the activity of hydrons in solution (antilog $(-H_0) = a_{\mathrm{H}^+}$) only if an activity coefficient term, $\log(\gamma_{\mathrm{BH}^+}/\gamma_{\mathrm{B}})$, vanishes (24, 33). This condition is approximately fulfilled in very dilute solutions of indicator (i.e., very large excess of acid, AH, over the indicator) if the conjugate acid of the indicator (BH^+) is present as free ions, but not if it is present as tight ion pairs. The acids which do not satisfy this requirement cannot be characterized by an acidity function; the name *non-Hammett acids* was proposed for these species (34, 35).

On a solid surface, where acidity is present in individual, isolated sites, the interaction with a base (indicator) is always stoichiometric. Even when only a fraction of sites are neutralized, that is, a deficit of base is added, the excess of sites cannot stabilize the anion formed at the reacting site in the way anion stabilization is provided in solution (36). In addition, the reaction forms a tight ion pair at the acid site. Thus, solid acids are non-Hammett acids *par excellence.* The H_0 values obtained for them by the usual procedure are theoretically meaningless and do not reflect their real acid strength. One can nonetheless use the determination of the hydronation equilibrium of appropriate indicator bases (*not* just the color change of indicators) conducted under carefully controlled conditions to compare the relative strengths of such acids, more or less on a one to one basis. Some measurements of this kind have been published (37).

Reaction of Adamantane on Sulfated Zirconia

From the foregoing analysis it appears that the discussions of mechanism and the rationalization of catalytic activity of SMOs available in literature are less than satisfactory. We decided, therefore, to undertake an investigation of the mechanism of the first interaction of a SMO with a saturated hydrocarbon and try to identify the first reaction intermediates. We chose for our study SZ because the consensus is that SZ has the highest acid strength among the materials of this kind (9).

The catalyst used in most experiments, SZ with 1.5–1.7% S and 101–107 m^2/g, was prepared by impregnation of zirconium hydroxide with a controlled amount of sulfuric acid (controlled impregnation technique, sample label SZC) (14) and calcination at 600°C. Once calcined, the material was thermally stable, as determined by calcining one sample twice, first at 550°, then at 600°C. There was no loss in catalytic activity of the material after the first and the second calcinations. We also used catalysts made by the impregnation of zirconium oxide (15). These materials had lower surface areas and retained less sulfur upon calcination (14). All catalyst samples were stored in glass vials and activated at 450°C just before use. The properties of the catalysts used are presented in Table 1.

Among the tests of catalytic activity in cationic reactions, the isomerization of saturated hydrocarbons is the most demanding. This reaction is most often accompanied by cracking, which complicates product analysis and also deactivates the catalyst, because the resulting olefin products are coke precursors. To minimize cracking, a reactant hydrocarbon lower than C_7 has to be used (38). Among these, reaction of butane (2l–2o, 9) and even that of pentane (9a, 39) are run in the gas phase, whereas the reaction of hexane produces a five-component mixture even in the absence of disproportionation and cracking products (38). We choose, therefore, the isomerization of methylcyclopentane (MCP) to cyclohexane as the test reaction (14):


[6]

In addition to the convenient analysis, the boiling points of reactant and product are such that we could run the reaction in liquid phase, with no need for any special or sophisticated reaction system (see Experimental).

The results of the MCP isomerization experiments with the catalysts used in this work are shown in Fig. 1. The materials prepared from $Zr(OH)_4$ (SZCH) are appreciably more active catalysts than those made from ZrO_2 (SZCO), in agreement with our earlier results (14). This activity difference cannot be ascribed to the difference in specific surface area, as can be seen from the values of specific rates given in the last column of Table 1 ($1.49 \pm 0.36 \times 10^{-2}$ and $0.275 + 0.005 \times 10^{-2}$ mmol/h · m^2 for SZCH and SZCO, respectively). It was also observed that the reaction is very clean; whereas cracking would form ring-opened products with the same number of carbon atoms or less, no other product than cyclohexane is seen even at long reaction time, when the isomer mixture approaches the equilibrium composition (40).

The absence of ring-opened products is mechanistically significant. It was shown that MCP is cleaved by HF–SbF_5 to hexyl cations ($C_6H_{13}^+$):

$$\mathrm{MCP} + \mathrm{AH} \rightarrow C_6H_{13}^+ + \mathrm{A}^- \qquad [7]$$

Hydride transfer leads then to tertiary methylcyclopentyl cations (MCP^+) and hexane isomers (C_6H_{14}) (41):

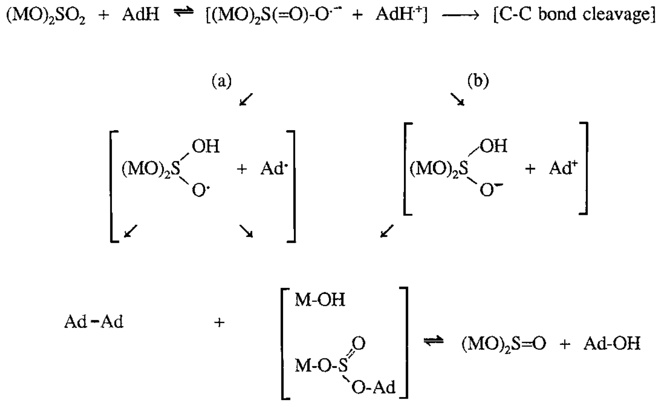
$$C_6H_{13}^+ + \mathrm{MCP} \rightarrow C_6H_{14} + \mathrm{MCP}^+ \qquad [8]$$

An alternative mechanism, by which MCP^+ is formed by hydron attack of the tertiary C–H bond with formation of hydrogen (42), was disproved by reaction of MCP with the nonoxidizing superacid HF–TaF_5 under hydrogen, when only $C_6H_{13}^+$ and C_6H_{14} were formed (43). Both alkyl and cycloalkyl cations serve to initiate the isomerization of a saturated hydrocarbon feed (41b). The absence of any C_6H_{14} products in the reaction mixture from isomerization of MCP on SZ suggests that a different mechanism than that encountered in superacid solutions intervenes here, at variance with the mechanistic models previously advanced for this catalyst (2, 3, 9).

An alternative mechanism consists of initiation by a one-electron transfer from substrate to catalyst, followed by cleavage of the radical cation thus formed by loss of a hydrogen atom or a free radical to form a carbocation which then initiates the isomerization reaction. The absence of ring-opening products shows that neither MCP^+ nor the cyclohexyl cations undergo β cleavage. Elimination and dimerization to $C_{12}H_{22}$ hydrocarbons (44) and then to heavier molecules probably occurs, because the catalyst becomes yellow after reaction, but the resulting heavy molecules do not crack, either.

Experimental data consonant with one-electron oxidation rather than acid–base interaction of strong acid catalysts exist. Thus, the ability of SbF_5 in superacids like HF–SbF_5 and FSO_3H–SbF_5 to oxidize hydrocarbons such as benzene (32a) or even alkanes (45) has been reported. Next, it was found that carbocationic isomerization and cracking can be initiated by a one-electron oxidation performed chemically (46) and that isomerization of alkanes in superacid solution is accelerated by a positively charged electrode (electrochemical oxidation) (47). On the other hand, it was shown that under somewhat extreme conditions (temperature-programmed desorption at 500–600°C) SZ can oxidize benzene and even pyridine all the way to CO_2 (48).

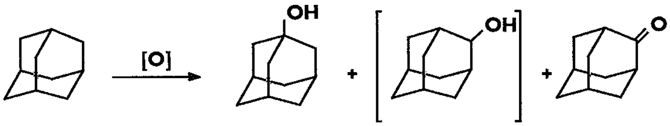
Assessing the nature of the first step in the reaction of a saturated hydrocarbon with an acid catalyst is difficult because the intermediate (chain-initiating species) formed in it reacts to give products which are not distinguishable from those formed in much larger amounts from the chain-propagating step. The idea to use a deficit of reactant such that the product from the first step is easier to analyze does not normally work because the reactant under such conditions is entirely broken up in small, gaseous fragments. We studied, therefore, the reaction of adamantane on SZ. Adamantane is thermodynamically very stable; it constitutes the final product of isomerization or even disproportionation of various C_{10} hydrocarbons (20). The corresponding cation, 1-Ad$^+$, even though it has a bridgehead cationic carbon, is also unusually stable for a saturated carbocation, because elimination is precluded by the Bredt rule; it was prepared and investigated even in the solid



SCHEME 1

state, as the fluoroantimonate salt (49). To identify the minute amounts of products of the first reaction with the catalyst, the latter was used in an amount close to equimolar, in contrast with the normal operation of catalytic hydrocarbon conversions.

Reaction of AdH on SZ (molar ratio AdH to S in SZ 1 : 3 to 1 : 1) was conducted in sealed tubes at several temperatures between 65 and 150°C. At the end of the reaction (2–6 days), the organic materials were extracted and analyzed by GC–MS. In most cases, the main reaction products were adamantanone (Ad$=$O) and 1-adamantanol (1-AdOH), as shown in Table 2. The isomeric alcohol, 2-adamantanol (2-AdOH) was not well separated from Ad$=$O on our column, but traces of it were tentatively evidenced in the tail of the ketone GC peak by the *m*/*z* 134 MS signal. The conversion amounted to a few percent of the starting material. Thus, the reaction is schematically described by:



[9]

Our results thus show that the reaction of SZ with AdH is an oxidation in which SZ is the electron acceptor. The one-electron acceptor ability of SZ was demonstrated before by an ESR spectroscopic study (2n). On the other hand, adamantane can be oxidized electrochemically to the corresponding cation radical ($AdH^{\cdot +}$) and to 1-Ad^+, which is then trapped by a nucleophile from solution (19). Oxidation is also achieved with an excess of sulfuric acid at 75°C, when Ad$=$O is formed in preparative yields (50).

A tentative mechanism for the oxidation of AdH on SZ is shown in Scheme 1. The symbol *M* represents the metal atoms which anchor the sulfate group to the solid. Both products of Scheme 1, the alcohol and the surface sulfite *M*O–S($=$O)–OAd, can ionize to form adamantyl cations. Both isomers 1-AdOH and 2-AdOH are formed in the reaction. The ketone, Ad$=$O, results from hydride abstraction by adamantyl cations from 2-AdOH or the corresponding surface sulfite esters (trapping of the carbocations by sulfate groups with formation of sulfate esters is also possible). This reaction is shown by

$$A^- + Ad^+ + 2\text{-}Ad{-}OH \rightarrow AH + AdH + Ad{=}O. \quad [10]$$

The formation of both 1-Ad^+ and 2-Ad^+ from the adamantyl cation ratical is not surprising. The two isomeric adamantyl free radicals resulting on path (a) of Scheme 1 have similar stabilities; on the other hand, the two isomeric adamantyl cations differ in stability by only 4 kcal/mol, an exceptionally small secondary vs tertiary carbocation difference (51). The two cations are, therefore, easily interconverting intramolecularly (50), or intermolecularly

$$1\text{-}Ad^+ + AdH \rightleftharpoons Ad{-}H + 2\text{-}Ad^+ \quad [11]$$

As 2-AdOH is oxidized (Eq. [10]), the hydride transfer equilibrium of Eq. [11] is displaced to the right.

It should be pointed out that formation of adamantyl cations is not in itself a proof of the oxidative mechanism of Scheme 1 An acidolysis of a C-H bond in AdH, like the one observed for isoparaffins in HF–SbF_5 (52), could also give adamantyl cations together with hydrogen. This mechanism was observed only for the strongest superacids, where persistent carbocations result (36a). By contrast, the SZ surface provides for nucleophiles strong enough to trap the transient Ad^+ as alcohols; therefore it is not strongly acidic enough for the acidolytic mechanism.

An unambiguous proof of the mechanism was provided by the observation and identification by GC–MS of small amounts of diadamantanes (Ad–Ad, at least two isomers) in the reaction product, as indicated in Scheme 1. Because of the high mechanistic significance of these products, we identified one of them by comparison of GLC retention time and mass spectrum with 1,1′-diadamantane synthesized independently (cf. Experimental). In contrast with the strong-acid-catalyzed reactions of simpler hydrocarbons, adamantane dimers cannot be formed by addition of a carbocation to an alkene, because the anti-Bredt alkene adamantene cannot be formed from Ad^+. Formation of diadamantanes is thus a proof not only of the one-electron oxidation pathway, but of the evolution of the pair of ion radicals by path (a) of Scheme 1. (We cannot exclude, however, path (b) as being responsible for a fraction of the products.)

Another product found in all experiments was methyladamantane (AdMe). Formation of this compound requires a complex succession of bond cleavage, coupling, and hydrogen transfer reactions. As shown in Table 2, the amount of AdMe relative to the simple oxidation products increased with temperature, which indicates that cleavage has a higher activation energy than oxidation. Dimethyl-, trimethyl-, and other alkyladamantanes were also observed when the reaction temperature increased. After reaction at 150°, only traces of oxidation products were observed in the mixture besides alkyladamantanes and heavy molecules, some containing adamantyl radicals easily lost in the MS (m/z 135), some not. As both cationic and free radical intermediates are involved, the reaction is necessarily complex, forming both heavy, polymeric products which color the catalyst from yellow to gray, and smaller fragments which recombine. The loss of adamantanone at 150°C shows that the latter undergoes further reaction on SZ, as proven by the disappearance of adamantanone from a 10 : 1 mixture of AdH and Ad=O after reaction on SZ at 135 and 150°C (see Experimental). It has to be reemphasized, however, that adamantane still remained the main component of the reaction mixture. A very small amount of a material of mass 168 exhibiting a strong Ad^+ fragment (m/z 135) was also observed in the mixture from the 150° reaction and was identified as 1-adamantanethiol (1-AdSH).

To reduce the extent of C–C bond cleavage reactions, the conversion at 150° was also run on a SZCH catalyst slightly deactivated by exposure to air for a few minutes between addition of AdH and sealing of the ampoule (in addition, the ampoule was not dried before the reactants were added). Ad=O and 1-AdSH were the main products and 1-AdOH was also formed. In addition, a small amount of adamantyl sulfide (Ad−S−Ad, mass 302) was observed. These products resulted from trapping of carbocations by sulfide or HS^- anions existing on the surface, for example:

$$M{-}\mathrm{SH} + \mathrm{Ad}^+ \rightarrow M^+ + \mathrm{Ad}{-}\mathrm{SH}. \qquad [12]$$

Similar results were obtained with two less active catalysts prepared from $\mathrm{ZrO_2}$ (SZCO), one containing 0.94% S, the other 1.55% S, except that in one of them (SZCO-0.95, Table 2) a very small amount of 2-AdSH was also identfied among the products.

Upon standing for a few weeks as a solution in acetone in the presence of air, the thiol peaks decreased in intensity and two new peaks of sulfur-containing compounds grew at much longer retention times. The mass spectra were consistent with disulfides (mass 334, base peak for Ad^+ at m/z 135, and the fragmentation pattern of the latter). The major peak was tentatively assigned to the disulfide corresponding to 1-AdSH (1-Ad–S–S–Ad-1), and the minor peak (not always seen) was most likely to isomer 1-Ad–S–S–Ad-2. Small amounts of disulfides were observed in the solutions immediately after extraction of products from the solid, but it is not clear whether they were formed during the reaction at 150°C or during the workup.

The reduction of sulfate by a hydrocarbon all the way to sulfide is remarkable, and to the best of our knowledge uprecedented (53). The reaction thus shows that bonding of sulfate groups to the surface of zirconia increases dramatically the oxidizing power of sulfur compounds.

The ^{13}C NMR spectrum of the mixture from the reaction with the air-exposed SZCH catalyst exhibited, in addition to the signals of compounds identified by GC–MS (e.g., adamantanone at 218 ppm) a broad signal centered at 128 ppm with two narrower peaks at 141 and 148 ppm, indicating that the polymeric products are largely aromatic. A very small peak at 188 ppm might be due to some cyclic, possibly polycyclic, carboxylic acid.

In oxidation of adamantane by $\mathrm{H_2SO_4}$ (50) or of alkanes by $\mathrm{FSO_3H}$ (54), sulfur dioxide was evolved from the mixture. The product resulting from the reduction of the SZ catalysts should be a sulfite group chemically bonded to the surface, because no $\mathrm{SO_2}$ was identified by smell or by GC–MS analysis of the gaseous phase after reaction. This is understandable, because even in the total oxidation of benzene by SZ sulfur dioxide is sometimes evolved at temperatures higher than 700°C, well after $\mathrm{CO_2}$ had been desorbed (48).

CONCLUSION

Reaction of sulfated zirconia with adamantane consists of a one-electron oxidation of the hydrocarbon with the formation of a cation radical. Hydron transfer to the surface anion radical leads to the adamantyl free radical ($\mathrm{Ad}^\cdot$) paired with the free radical site on the surface. These can combine to a surface sulfite ester, which was not identified. This ester or the free radical pair is converted to the corresponding alcohol (1- or 2-adamantanol). The bridgehead alcohol remained at the end of the reaction in large enough quantities to be identified. A fraction of the adamantyl radicals diffuses on the surface and dimerizes to diadamantanes (at least two isomers).

The surface sulfites or the alcohols, or both, are the precursors of adamantyl cations on the surface. Hydride transfers convert almost all 2-adamantanol to the ketone, adamantanone. It is possible that the carbocations are formed in part directly from the radical cation/radical anion pair, by the transfer of a hydrogen atom from the former to the latter.

The reduced sulfur remains on the surface, possibly as bonded sulfite groups; no $\mathrm{SO_2}$ was observed among the reaction products. At 150°C, reduction of sulfate by the hydrocarbon goes in part to sulfide, which reacts with Ad^+ and forms 1-AdSH and 2-AdSH. This exceptional reaction attests to the dramatic increase in oxidizing ability of sulfate when boned to the zirconia surface. Carbon–carbon bond cleavage, recombination, and hyrogen transfer lead to a series of volatile products, among which methyl-substituted adamantanes are prominent, and to some heavy aromatic structures. These reactions have a higher activation energy than the oxidation and dominate the reaction at 150°C.

Our findings are relevant for the mechanism of hydrocarbon conversions (cracking, isomerization) catalyzed by SZ. Our experiments were purposely conducted at temperatures within the range of the use of SZ as catalyst. As a matter of fact, alkane isomerization on SZ has been in most cases conducted at temperatures such as 150°C (2o, 2p, 10), 200°C (38), 250°C (2l–2n, 15), and even 300°C (2m, 55), equal to or higher than the temperatures at which AdH reduces SZ all the way to sulfide. The high catalytic activity of SZ can be ascribed to its exceptional activity as a one-electron oxidizing agent for hydrocarbons, generating cation radicals which are converted to sulfite and sulfate esters on the surface. The latter form carbocations by ionization or by elimination of olefins followed by hydronation and thus initiate the reaction. The acidity of the catalyst needs to be just strong enough to allow the reaction to continue by a cationic or cationoidic (that is, via weakly coordinated carbocations) mechanism from the surface esters or olefins. It should be pointed out that work linking deactivation of SZ to reduction of S(VI) and reactivation to reoxidation of sulfur was reported (55).

Previous authors have related the one-electron donor ability with acidity. This representation is not correct. As emphasized before, in both Lewis and Brønsted acid–base interactions, the transfer of electrons from base to acid occurs together with the formation of a covalent bond. *If there is no covalent bond formed, the reaction is not acid–base, but oxidation–reduction* (34, 56).

APPENDIX

MS Splitting Patterns of the Main Products

1-Methyladamantane (1-AdCH$_3$): $m/z = 150$ ($M^{\cdot +}$), 13.25%; 135, 100%; 107, 9.48%; 93, 30.34%; 81, 5.39%; 80, 3.01%; 79, 23.13%; 78, 2.41%; 55, 5.54%; 41, 13.58%. (The literature spectrum is quite similar, only m/z 79 is more intense than m/z 93) (16).

1,3-Dimethyladamantane (1,3-Ad(CH$_3$)$_2$): $m/z = 164$ ($M^{\cdot +}$), 8.86%; 149, 100%; 121, 3.31%; 107, 14.94%; 93, 25.82%; 91, 8.27%; 81, 5.22%; 79, 8.65%; 77, 6.92%; 65, 3.17%; 63, 0.50%; 55, 6.23%; 53, 4.90%; 41, 14.27%; 39, 10.40% (identified by comparison with an authentic sample).

Trimethyladamantane (Ad(CH$_3$)$_3$: $m/z = 178$ ($M^{\cdot +}$), 8%; 177, 3.8%; 163, 100%; 135, 1.85%; 121, 12.15%; 107, 61.58%; 105, 4.02%; 95, 5.68%; 93, 12.18%; 91, 11%; 81, 7.17%; 79, 8.84%; 77, 6.65%; 69, 4.44%; 67, 5.87%; 65, 3.37%; 55, 9.67%; 53, 5.16%; 43, 3.51%; 41, 18.37%; 39, 8.26% (no reference available).

1-Adamantanol (1-AdOH): $m/z = 152$ ($M^{\cdot +}$), 14,70%; 95, 100%; 94, 14.35%; 79, 8.30%; 67, 6.85%; 55, 6.77%; 41, 14%; 39, 9.97% (identified by comparison with an authentic sample).

Adamantanone (Ad=O): $m/z = 150$ ($M^{\cdot +}$), 100%; 132, 4.49%; 117, 18.29%; 107, 4.79%; 104, 10.76%; 93, 12.29%; 91, 13.44%; 81, 31.97%; 80, 60.27%; 79, 74.24%; 78, 17.71%; 77, 13.84%; 72, 14.65%; 68, 5.08%; 67, 12.12%; 66, 7.70%; 65, 5.52%; 57, 4.80%; 56, 0.42%; 55, 7.98%, 54, 11.39%; 53, 11.51%; 41, 21.41%; 39, 22.24%; 27, 16.20% (identified by comparison with an authentic sample).

1-Adamantanethiol (1-AdSH):$m/z = 168$ ($M^{\cdot +}$), 8.61%; 136, 10.66%; 135, 100%; 134, <0.5%; 107, 9.11%, 93, 21.35%; 91, 9.28%; 81, 6.93%; 79, 26.16%; 77, 9.94%; 69, 2.84%; 67, 10.66%; 65, 4.72%; 55, 6.30%; 53, 4.97%; 51, 2.62%; 45, 2.73%; 41, 11.14%; 39, 10.35%, in agreement with the published spectrum (17).

2-Adamantanethiol (2-AdSH): $m/z = 168$ ($M^{\cdot +}$), 24.5%; 135, 100%; 93, 36.4%; 91, 29.1%; 81, 27.3%; 79, 54.5%; 77, 27.3%; 67, 45.4%; 41, 36.4%; 39, 36.4%. Because the amount of this compound in the mixture was very small and the peak intensities were measured on the recorded spectrum, the intensities given are approximate. In agreement with the literature (17), the spectrum is very similar to that of 1-AdSH, with the exception of the intensity ratios of m/z 168 and 135, and of m/z 93 and 91.

1,1′-Diadamantane (1,1′-Ad–Ad): $m/z = 270$ ($M^{\cdot +}$), 8.97%; 214, 0.14%; 155; 0.31%; 135, 100%; 134, 57.87%; 119, 2.96%; 93, 11.24%; 92, 6.96%; 91, 6.00%; 81, 3.00% 79, 15.14%; 77, 4.72%, 67, 4.94%; 65, 1.2%; 55, 3.12%; 53, 1.48%; 41, 4.67%; 39, 1.30% (identical with the spectrum of the synthetic sample).

Diadamantyl sulfide (Ad–S–Ad, presumed 1,1′): $m/z = 302$ ($M^{\cdot +}$), 12.71%, 135, 100%, 107, 11.41%, 93, 22.07%, 91, 15.28%, 81, 10.10%, 79, 32.26%, 77, 14.95%, 67, 17.01%, 65, 3.92%, 55, 10.35%, 53, 5.55%, 41, 17.38%, 39, 6.25% (no reference available).

Diadamantyl disulfide (Ad–S–S–Ad, major, presumed 1,1′): $m/z = 334$ ($M^{\cdot +}$), 5.05%; 167, 0.48%; 135, 100%; 107, 8.03%; 105, 1.72%; 93, 17.65%; 91, 7.71%; 81, 5.17%; 79, 19.78%; 77, 7.48%; 69, 1.78%; 67, 8.93%; 65, 2.48%; 55, 6.02%; 53, 3.33%; 41. 9.74%; 39, 2.79% (no reference available).

Diadamantyl disulfide (Ad–S–S–Ad, minor, presumed 1,2′): $m/z = 334$ ($M^{\cdot +}$), 4.43%; 149, 2.18%; 135, 100%; 107, 9.94%; 105, 2.76%; 93, 20.13%; 91, 11.78%; 81, 6.79%; 79, 27..08%; 77, 9.20%; 67, 15.23%; 65, 3.88%; 55, 10.50%; 53, 5.56%; 41, 13.62%; 39, 4.58% (no reference available).

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