

Homolytic C–S Bond Cleavage on a Heterogeneous Co/Mo/S Hydrodesulfurization Catalyst

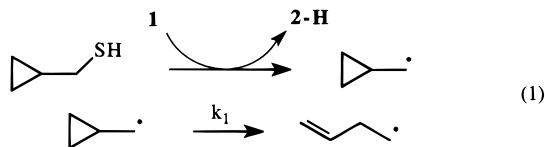
Keenan E. Dungey and M. David Curtis*

Willard H. Dow Laboratory, Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109-1055

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The hydrodesulfurization (HDS) of petroleum is an industrially important catalytic process whose mechanism still remains elusive.¹ Organometallic reactions² and reactions on single-crystal surfaces³ have been used to model HDS catalysts and possible mechanisms. Recent work of Bianchini *et al.* has demonstrated the first HDS catalyst by a homogeneous system.⁴ However, few parallels between model systems and the actual Co/Mo/S catalysts have been made.^{2,5} We wish to report the first direct comparison of an organometallic desulfurization reaction with the reactivity of a heterogeneous HDS catalyst.

Previously, we reported that **1'**, Cp₂Mo₂Co₂S₃(CO)₄ (Cp' = η⁵-C₅H₄Me), desulfurized organic thiols and sulfides in solution to form the cluster Cp₂Mo₂Co₂S₄(CO)₂ (**2'**) and the corresponding hydrocarbon.⁶ A kinetic study revealed that binding of the thiol to cluster **1'** was the rate-determining step in the desulfurization reaction and that the C–S bond was cleaved homolytically.⁷ Proof of a radical intermediate was furnished by the reaction of cyclopropylmethylthiol (CPMT) with the cluster **1'**. The organic product was 1-butene, arising from the rearrangement of the cyclopropylmethyl radical to the butenyl radical which then abstracted an H atom (eq 1). This rearrangement



occurs at a known rate ($k_1 = 1.3 \times 10^8/s$ at 25 °C) and is characteristic of a free radical clock reaction.⁸ We now report that the reaction of cluster **1** (Cp = η⁵-C₅H₅) with a slower radical clock, 5-hexene-1-thiol ($k_2 = 1.0 \times 10^5/s$ at 25 °C), also produced the characteristic free radical rearrangement product, methylcyclopentane (eq 2).⁹

Having demonstrated C–S bond homolysis as the desulfurization mechanism in this model system, we desired to explore whether or not this mechanism applied to the actual HDS

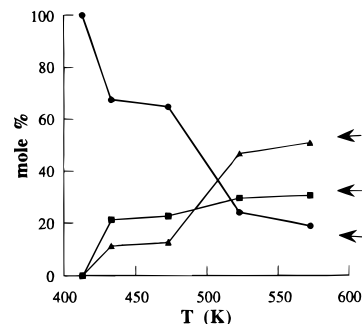
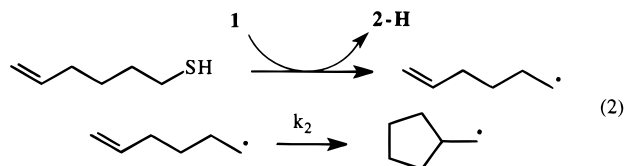


Figure 1. Normalized 1-butene (●), *cis*-2-butene (■) and *trans*-2-butene (▲) products from the HDS of CPMT (arrows indicate the equilibrium concentrations of the respective butenes at 600 K).

catalyst. A Co-promoted MoS₂ HDS catalyst supported on γ-alumina was loaded into a differential flow reactor and



activated in the usual manner.¹⁰ A solution of CPMT¹¹ was injected into a stream of hydrogen gas at 1 atm pressure and passed over the heated catalyst. At 300 °C, almost complete conversion of the thiol was observed, and the hydrocarbon products were a mixture of butene isomers in their thermodynamic ratios and a small amount of propene (Figure 1; Table 1, Supporting Information).¹² The conversion was varied by lowering the temperature. The change in product distribution to 100% 1-butene at 140 °C (Figure 1, Table 1) indicates that the initial product of the HDS reaction is 1-butene, which is then isomerized to the other thermodynamically favored butene isomers. No methylcyclopropane (MCP) was detected.

In a control experiment, MCP in a hydrogen stream at 1 atm pressure was passed over the catalyst bed. In addition to unreacted MCP, the products at 140 °C were 33% 1-butene, 44% *cis*-2-butene, and 23% *trans*-2-butene. The 1-butene was present in large excess of its thermodynamic ratio: 1.0:1.3:0.7 (obsd) vs 1.0:5.0:10.0 (equilibrium) for 1-butene/*cis*-2-butene/*trans*-2-butene (Table 1). It has been shown that MCP thermally rearranges by C–C bond homolysis, followed by H-atom shift,¹³ and the ratio of the *cis*- to *trans*-2-butene products was approximately 2,¹⁴ as seen here. These results clearly show that the product slate observed in the HDS of CPMT does not come from the isomerization of initially formed MCP but is consistent with the formation and rearrangement of the cyclopropylmethyl radical in the HDS process.

(10) MoO₃ (14%, 0.040g) and CoO (3.5%) supported on alumina (Strem) was diluted to 1% metal loading by mixing with γ-Al₂O₃ (0.676 g) (Catapal). This plug of catalyst loosely filled a 0.5 cm i.d. glass tube to a depth of 1 cm, where it was reduced at 400 °C in H₂ (20 cm³/min) for 4 h, followed by sulfiding for 4 h at 400 °C in 10% H₂S/H₂ (total flow 20 cm³/min).

(11) Prepared by S. H. Druker following the procedure of Cossar (Cossar, B. C.; Fournier, J. O.; Fields, D. L.; Reynolds, D. D. *J. Org. Chem.* **1962**, *27*, 93). A solution in benzene-*d*₆ (0.2 M) was injected into the heated region of a differential flow reactor at a rate of approximately 0.1 mL/h. The reactor was loaded as described above and the carrier gas was H₂ (20 cm³/min). Products were analyzed by GC (PE 8400, 8 ft × 1/8 in., 0.19% picric acid on Carbowax-C), quantified by a standardized gas mix (Scott Specialty Gases), and verified by GC/MS and ¹H NMR.

(12) Thermodynamic ratios calculated at 600 K from American Petroleum Institute (API) tables. Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimental, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, PA, 1953.

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(9) In an inert atmosphere box, a resealable NMR tube was charged with **1** (23mg, 35 μmol), toluene-*d*₈ (1 mL), and 5-hexene-1-thiol (3 mL, 26 μmol), sealed, and removed. The mixture was heated to reflux for 10 h, while ¹H-NMR spectra were taken periodically to monitor the reaction progress. Compound **1** was converted to **2** almost quantitatively, while the thiol was desulfurized, forming methylcyclopentane, as indicated by the doublet at δ 0.95 (in toluene-*d*₈). GC/MS of the head gases had one peak with *m/e* = 69 and 56.

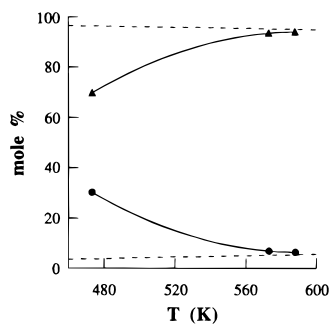


Figure 2. Normalized 1-hexene (●) and internal hexenes (▲) yields from the HDS of 5-hexene-1-thiol (dashed lines indicate the equilibrium concentrations of the respective hexenes).

The hydrodesulfurization of 5-hexenethiol by the heterogeneous catalyst was also performed,¹⁵ and in this case the product was not that expected from free radical rearrangement (Table 2, Supporting Information). At 200 °C, the conversion was low, and the products were internal hexenes (62 mol %) and 1-hexene (27 mol %), the latter in excess of its thermodynamic ratio (equilibrium: 94% internal/6% terminal). Some hydrogenation product (hexane) was observed but no methylcyclopentane was detected. As the reaction temperature was raised, the product slate approached the equilibrium ratios (Figure 2).¹⁶ In control experiments, 1-hexene was quickly isomerized to internal hexenes, while methylcyclopentane showed no rearrangement. The product distribution is consistent with the initial formation of 1-hexene, followed by isomerization to the thermodynamically favored internal hexenes.

A mechanism for the heterogeneous HDS of the free radical clocks is presented in Scheme 1. This mechanism parallels that proposed for the homogeneous desulfurization of thiols by cluster **1'**. The steps include adsorption of the thiol on the surface, homolytic C–S bond cleavage, and rearrangement of the resulting radical. For cyclopropylmethyl radical, this occurs faster than hydrogenation of the radical, presumably by a hydrogen atom on the surface of the catalyst. The results of the HDS of 5-hexenethiol can also be explained by Scheme 1 if the rate of hydrogenation is greater than the rate of cyclization of the 5-hexenyl radical ($k_2 = 1.5 \times 10^7/s$ at 300 °C).¹⁷ We recognize that other mechanisms are possible (e.g., initial hydrogenation of the olefin, E2 elimination of the thiol to produce 1-hexene, followed by isomerization to internal hexenes) and experiments are underway in our lab to address these issues.

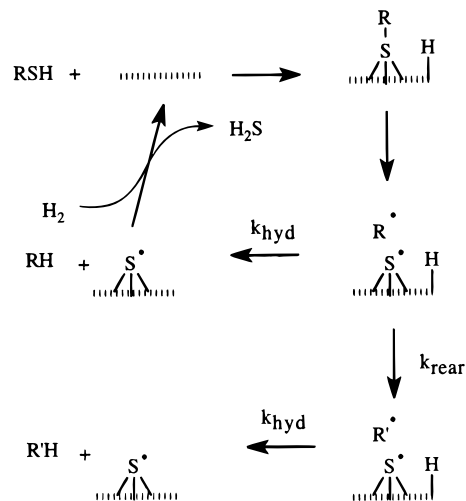
The difference in reactivity between the cluster model and the heterogeneous catalyst may stem from the drastic differences in conditions. The concentration and reaction rate of hydrogen atom sources (metal hydrides or thiols) should be very different from solution state to heterogeneous systems, resulting in

(15) A 0.28 mM solution of 5-hexenethiol (for preparation, see: Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262) in toluene was injected via syringe into the heated zone of the differential flow reactor at approx. 0.1 mL/h. The reactor was loaded with 0.36 g of catalyst and the carrier gas was H₂ (10 cm³/min). Products were analyzed as described above.¹¹

(16) Equilibrium calculated from API tables.¹²

(17) Calculated from tables in ref 8.

Scheme 1



different rates of hydrogen abstraction. For example, if metal hydrides are the hydrogen donors on the surface of the heterogeneous catalyst (as presumed in Scheme 1), we would expect the reaction rate with formed radical to be greater than the rate of hydrogen abstraction from thiols in solution, based on organometallic models.¹⁸

The formation of free radicals in the vicinity of surfaces has been explored under UHV (ultrahigh vacuum) conditions with alkyl halides and metal crystals.¹⁹ Recently, a study of the desulfurization of cyclopropylmethylthiol on a Mo(110) crystal was performed under UHV conditions.²⁰ Homolytic cleavage was proposed as the mechanism for the C–S bond cleavage on the surface, but no rearrangement products typical of the cyclopropylmethyl radical were observed. The lack of rearrangement products was rationalized by assuming that C–S bond breaking and C–H bond forming were nearly simultaneous (at least the hydrogenation occurred at a much faster rate than the radical rearrangement). We have demonstrated here that this is not the case for the HDS of CPMT over a conventional catalyst operating at the usual temperatures and atmospheric pressure. It appears that in this particular case, at least, an organometallic cluster in solution models the heterogeneous catalyst better than a clean metal surface under UHV conditions.

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Supporting Information Available: Tables of product distribution (1 page). See any current masthead page for ordering and Internet access instructions.

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