JOURNAL OF CATALYSIS 97, 252–260 (1986)

Catalytic Hydrodesulfurization of *o*-Aminobenzyl Sulfides

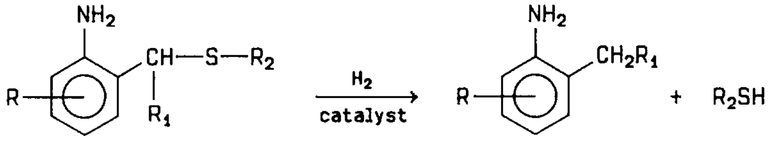
Hydrodesulfurization of *ortho*-aminobenzylsulfides to *ortho*-alkylanilines with particular attention to the reaction of 2-methylthiomethyl-6-trifluoromethylaniline to 2-methyl-6-trifluoromethylaniline has been examined in a batch reactor at 453–473 K (180–200°C) and hydrogen pressures between 1034 and 13,785 kPA (150–2000 psi). Application of typical hydroprocessing catalysts, such as sulfided CoO-MoO_3/γ-Al_2O_3, fails to retain the substituent groups while selectively cleaving the carbon–sulfur bonds. Use of sulfided CoO–MoO_3-on-carbon and various unsupported, sulfided $Co_xMo_yO_z$ catalysts with x/y in the range 1/4 to 4/1 gives high selectivity to the organic product. An abbreviated kinetic study using unsupported, presulfided $CoMoO_4$ shows that the reaction rate is first order with respect to the gas and liquid reactant with no noticeable inhibition effects. Comparisons between reaction rates for this reaction to those for typical petroleum hydrodesulfurization reactions show that the current system proceeds at significantly lower temperatures with an order-of-magnitude higher rates.

INTRODUCTION

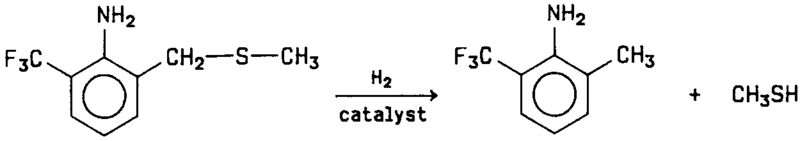
Catalytic desulfurization and reduction of organic sulfides to hydrocarbons and thiols occupies an important position in applications ranging from laboratory-scale synthesis (*1–6*) to commercial hydroprocessing of petroleum fractions (*7–9*). The wide range of applications encountered in these and related studies has resulted in the development of various diverse methods for desulfurization which are summarized in detail elsewhere (*2*). Of these various methods, those based upon heterogeneous catalysts such as Raney nickel (*10–12*), Raney cobalt (*13*), and alumina-supported cobalt-molybdate and related oxides (*7–9, 14–15*) have the most widespread application. Use of Raney nickel and its modified forms can have several drawbacks which include: (i) the undesired reduction of olefinic double bonds, carbonyl and nitro groups (*16*); (ii) the promotion of undesired side reactions (*17*); (iii) difficulties associated with handling since it is pyrophoric, and (iv) is readily available in powdered form but not in tableted form. These features suggest that the choice of a suitable heterogeneous catalyst for pilot or commercial-scale processing of nonpetroleum type organics is directed toward use of the alumina-supported metallic oxide or sulfide catalysts as encountered in the petroleum industry.

The principal chemical reaction that occurs in petroleum hydrodesulfurization is basically limited to cleavage of simple carbon–sulfur bonds followed by hydrogen saturation of the free valencies and of olefinic double bonds (*7–9*). This represents a marked contrast to a particular class of reactions that have recently arisen in chemical processing (*18*) involving cleaving of carbon–sulfur bonds that are present as substituent groups on an aromatic structure where a high yield of a specific organic product is desired. The particular reaction of interest in this work involves the conversion of *ortho*-aminobenzylsulfides to *ortho*-alkylanilines written generally as

0021-9517/86 $3.00


[1]

In this reaction, R can represent alkoxy, alkyl, alkenyl, haloalkyl, halogen, hydroxy, or hydrogen, R_1 can represent alkyl, alkenyl, or hydrogen, while R_2 can represent alkyl, alkenyl, aryl, or hydrogen. The reaction of particular interest here involves the conversion of 2-methylthiomethyl-6-trifluoromethyl aniline (abbreviated here as MT_2MA) in the presence of hydrogen and a suitable catalyst to yield 2-methyl-6-trifluoromethylaniline (abbreviated here as MTMA) where $R = CF_3$, $R_1 = H$, and $R_2 = CH_3$:


[2]

Particularly noteworthy is that application of petroleum hydrodesulfurization catalysts would be expected to be unsuccessful for the reaction given by Reaction [2] since these types of catalysts have been shown to react with the carbon–fluorine bond of trifluoromethylbenzene ($C_6H_5CF_3$) and incorporate the fluorine ion into the catalyst (*19*). Hydrodesulfurization of related compounds within the classification of Reaction [1] having other types of functional groups as part of an effort to assess their sensitivity to reaction conditions and catalyst type is in progress.

One objective of this note is to show that typical supported petroleum hydroprocessing catalysts are unsuitable for selective carbon–sulfur bond cleavage for the *ortho*-aminobenzyl sulfide given in Reaction [2]. Another objective is to define suitable heterogeneous catalysts for laboratory synthesis and commercial processing that give high yields of the organic product. A final objective is to briefly summarize some kinetic results for Reaction [2] and to point out some differences and similarities between this type of hydrodesulfurization versus petroleum hydrodesulfurization. Additional details related to these objectives and other aspects related to this investigation will be given in a future publication (*20*).

EXPERIMENTAL

Most of the hydrodesulfurization experiments were performed using a 0.3-liter stainless-steel Autoclave engineers reactor with appropriate controls for reactor temperature and pressure. Liquid-phase samples could be obtained during the course of a run by withdrawal through a 1.5875-mm o.d. (0.0625 in.) × 0.762-mm i.d. (0.03 in.) capillary tubing and a suitable valve arrangement. Liquid reactant and catalyst in the form of a powder was charged to the reactor in the presence of argon to minimize exposure to air. Air was further excluded from the reactor by flushing the reactor with hydrogen several times after sealing. The results given here correspond to hydrogen pressures between 1034 and 13,785 kPa (150–2000 psig), reaction temperatures between 453 and 473 K (180–200°C), catalyst loadings of ca. 4 wt%, and initial MT_2MA concentrations of less than

10 wt% with toluene as the inert reaction solvent. A wider range of conditions to further define the scope and limitations of this system including discrimination between various reaction mechanisms by analysis of the associated reaction rate expressions is given elsewhere (*20*).

Quantitative analysis of the liquid-phase reaction products was performed using a Varian 3700 gas chromatograph with dual thermal conductivity detectors. Analysis of toluene, *ortho*-trifluoromethylaniline (OABT), 2-methyl-6-trifluoromethylaniline (MTMA), and 2-methylthiomethyl-6-trifluoromethylaniline (MT_2MA) was performed using a 1 m × 3.175 mm (0.125 in.) stainless-steel column packed with 3% OV-101 on 80/100 Chromosorb W. Analysis of hydrogen sulfide (H_2S), methylmercaptan (MESH), dimethylsulfide (DMS), and other low-boiling thiols was performed using a column of the same dimensions but packed with 80/100 mesh Porapak Q. The columns were connected through a Carle switching valve with appropriate sequencing so that a complete analysis of the liquid phase could be performed using a single 2-μl injection. Calibration was performed using dodecane as the internal standard with response factors being determined using calibration solutions. Quantitative analysis of a reactor head gas sample was performed for a few selected runs after reactor cool down using a Carle Series SX fixed gas analyzer.

Catalyst precursors used to obtain the results given here included commercially available petroleum HDS catalysts such as Nalco 477 (3.3% CoO and 14.0% MoO_3 on γ-Al_2O_3), a carbon-supported CoO–MoO_3 catalyst, and various unsupported $Co_xMo_yO_z$ catalysts where the x/y ratio was varied between 1/4 and 4/1. In one case reported here, the Nalco catalyst was modified by treatment with a ca. 3 *N* potassium hydroxide solution to neutralize the acidic sites. The carbon-supported catalyst was prepared by step-addition and coimpregnation with aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_3 \cdot 6H_2O$ with calcinations of 383 and 723 K, respectively. The final loading was 3 wt% Co and 13 wt% Mo. The various $Co_xMo_yO_z$ catalysts were prepared by mixing aqueous solutions containing appropriate amounts of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ and evaporating the mixture to dryness. Calcination of the dried catalyst was performed for 5 h at 738 K.

All catalyst precursors were presulfided in a quartz-glass dip-tube reactor using a hydrogen stream containing 10% hydrogen sulfide at 523 K for 1 h beyond breakthrough of H_2S.

Detailed physical and chemical characterization of all catalyst samples was performed also but is omitted here for brevity and will be given in a future publication (*20*).

The sulfide reactant given in Reaction [2] was prepared using the organic synthesis procedure given by Claus and Vycudilik (*21*). Positive identification of this and other species was performed using GCMS, F^{19} NMR, and H^1 NMR.

RESULTS AND DISCUSSION

Table 1 gives the selectivity to the desired product MTMA as a function of MT_2MA conversion for the catalyst precursors mentioned above as well as a few catalyst supports. Direct application of the Nalco 477 catalyst and other similar petroleum HDS catalysts generally give low selectivity to MTMA due to polymer formation. Attempts to neutralize the acidic support using potassium hydroxide gave similar results. Runs performed with various catalyst supports such as γ-Al_2O_3, which is a solid acid, and MgO, which is basic, convert MT_2MA to undesirable products, while the carbon support was essentially inert under the indicated reaction conditions. Both the acidity and basicity of commercial petroleum HDS catalysts and related catalyst supports, including the affinity of the metal oxides for the fluoride ion, are possible causes for poor selectivity of MT_2MA to MTMA.

TABLE 1

Experimental Result for Various HDS Catalysts

Catalyst	Initial MT_2MA concentration (wt%)	Hydrogen pressure (psig)	Reaction temperature (°C)	Reaction time (h)	% Conversion of MT_2MA (X)	% Selectivity to MTMA, (S)
Nalco 477	8	150	190	16.5	59.8	5.6
	7	2000	200	4	33	16.5
Nalco 477 + 20% KOH	13.2	130	180	15	18.2	0
Alcoa γ-Al_2O_3	7	150	195	16	63.8	0.7
MgO	7	150	195	16	23.6	3.4
Carbon	7	2000	200	5	0	0
Co–Mo/carbon	7.5	2000	200	3	94.8	>95
$CoMoO_4$	7.5	2000	200	4	90.7	99.2
$CoMo_2O_4$	7.5	2000	200	4	53.7	98.1
$CoMo_4O_4$	7.5	2000	200	4	50.2	97.9
$Co_2Mo_1O_4$	7.5	2000	200	4	53.7	94.8
$Co_4Mo_1O_4$	7.5	2000	200	4	95.2	97.0

Note. $X = \frac{N_{BO} - N_B}{N_{BO}} \times 100$; $S = \frac{N_{PO} + N_P}{N_{BO} - N_B} \times 100$; $w_c = 4$ wt%.

Application of the 3% CoO–13% MoO_3 on-carbon catalyst gave a MT_2MA conversion of 95% with greater than 95% selectivity to MTMA which represents a significant improvement when compared to the previously cited results.

The results of using unsupported cobalt–molybdenum oxides with Co/Mo ratios in the range from 1/4 to 4/1 show that all of these lead to high selectivity to the organic product MTMA with Co/Mo ratios of 1/1 and 4/1 giving the highest conversion. The same powder was pressed into 4.76 ×4.76-mm pellets using a Pennwalt–Stokes tablet machine with an average crush strength between 34.475 kPa (5 psi) and 55.16 kPa (8 psi) and used in basket reactor experiments with similar excellent results.

From the above results, one can conclude that either a carbon-supported Co–Mo catalyst or an unsupported $CoMoO_4$ powder or tablet are effective heterogeneous catalysts for selective cleavage of the carbon–sulfur bond in MT_2MA whereas petroleum HDS catalysts lead to poor results.

The reaction kinetics of MT_2MA hydrodesulfurization to MTMA using unsupported $CoMoO_4$ catalyst powder as the precursor were briefly investigated for comparison to typical petroleum HDS results such as those given by Gates and coworkers (*22–24*). Interpretation of the reaction kinetics is simplified when reaction rate inhibition due to various adsorbed species does not occur. For this case, the terms present in the denominators of various Langmuir–Hinshelwood or Eley–Rideal type rate expressions such as those tabulated in Tables 4–8 in (*24*) all reduce to unity. If the rate-determining step is assumed to be reaction between adsorbed hydrogen and MT_2MA, the intrinsic rate of reaction defined on a catalyst weight basis can be given as

$$-\frac{1}{w_c}\frac{dN_B}{dt} = kC_AC_B, \qquad (1)$$

where C denotes the surface concentration, N represents the number of moles, w_c denotes the catalyst weight, t denotes time, and the subscripts A and B refer to hydrogen and MT_2MA, respectively. If one as-

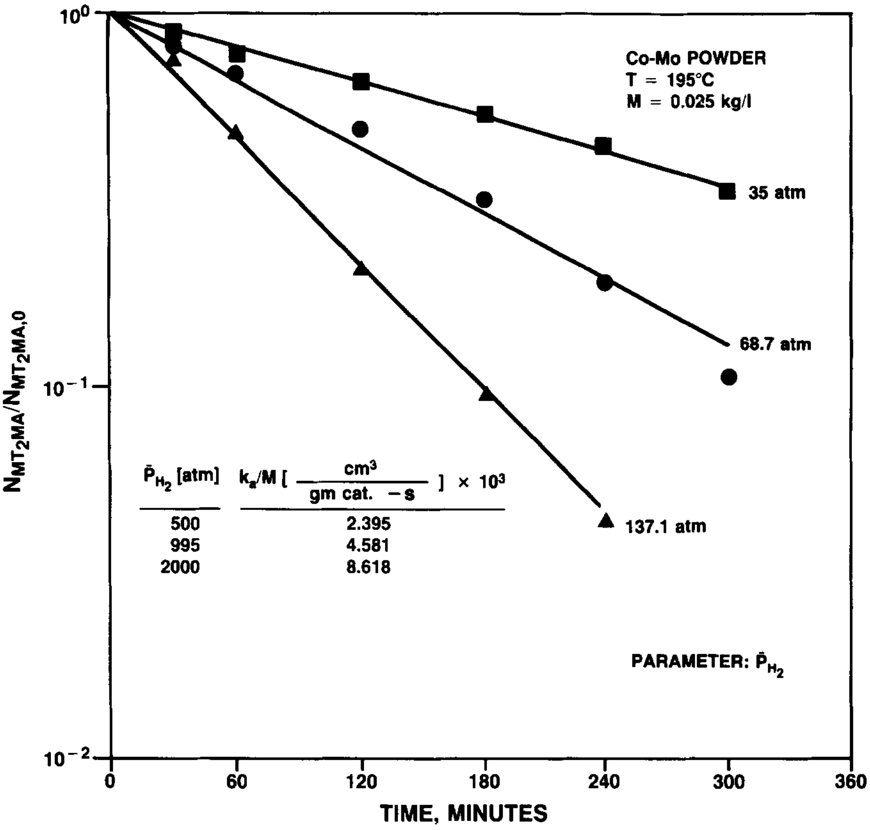


FIG. 1. Determination of pseudo-first-order rate constants at various hydrogen partial pressures.

sumes that the solubility of hydrogen in the liquid does not change appreciably as the concentration of the liquid phase changes, then a fixed Henry's law constant can be used to express the concentration of hydrogen in the liquid to its partial pressure in the gas phase as shown by

$$\bar{p}_A = H_A C_A. \qquad (2)$$

Substitution of Eq. (2) into Eq. (1) followed by integration of the resulting expression, assuming $\bar{p}_A$ is constant, yields the following familiar first-order batch reactor performance equation

$$-\ln \frac{N_B}{N_{BO}} = k_a t. \qquad (3)$$

The variable k_a denotes a pseudo-first-order reaction rate constant that can be related to hydrogen partial pressure $\bar{p}_A$ by Eq. (4) where $k' = k/H_a$ is introduced as a lumped second-order rate constant:

$$\frac{k_a}{M} = k'\bar{p}_A. \qquad (4)$$

The parameter $M = w_c/V_L$ denotes the catalyst loading where w_c is the catalyst weight and V_L denotes the liquid volume.

Reaction data obtained at hydrogen pressures of 500, 995, and 2000 psig (35, 68.7, and 137.1 atm absolute) are plotted in Fig. 1 according to the form suggested by Eq. (3). This verifies that the reaction rate exhibits first-order dependence on MT_2MA for the indicated range of conditions. A comparison between predicted and experimental values of N_B/N_{BO} as a function of reaction time using the rate constants from Fig. 1 is given in Fig. 2 where the agreement is quite satisfactory. Values of k_a/M obtained from

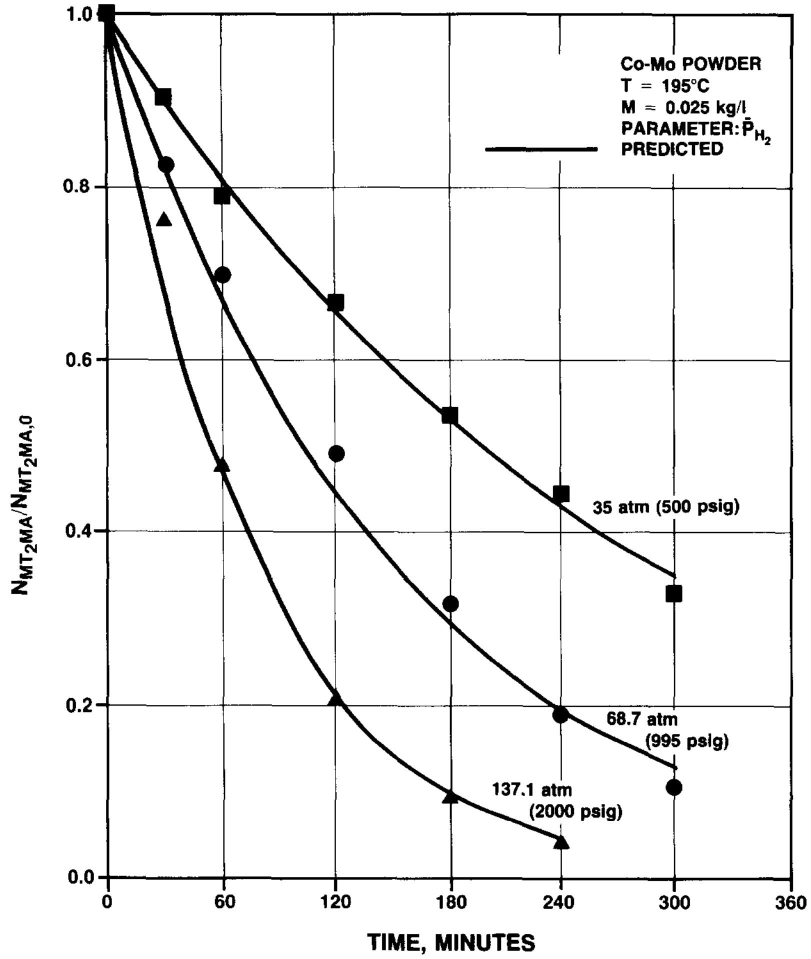


FIG. 2. Comparison between experimental and predicted values of normalized MT_2MA concentration versus time.

the slopes of the lines in Fig. 1 are plotted as a function of hydrogen partial pressure in Fig. 3 according to the form given by Eq. (4) which, analogous to Eq. (3), verifies that the reaction rate exhibits a first-order dependence on hydrogen concentration. The expression for the reaction rate given by Eq. (1) can, therefore, be written in terms of the observables w_c, $\bar{p}_A$, and C_B as

$$-\frac{1}{w_c} = 6.475 \times 10^{-5}\bar{p}_A C_B. \quad (5)$$

Equation (5) is valid for $T = 468$ K (195°C), $35 \leq \bar{p}_A \leq 137$ atm, and $0 \leq C_B \leq 7.5$ wt%. Development of an appropriate equation for the rate which is valid over a wider range of temperature, pressure, and concentration is complex enough to be the subject of a separate investigation and is omitted here for brevity.

The intrinsic reaction rate expression given by Eq. (5) assumes that the solubility of hydrogen in the liquid phase is proportional to the hydrogen gas pressure and is independent of liquid reactant and product concentrations according to Eq. (2). Examples are available (*25–27*) where the solubility of the gaseous reactant is dependent upon the liquid-phase composition. In these cases, the gas solubility must be related to the liquid-phase composition, pressure, and temperature before discrimination between

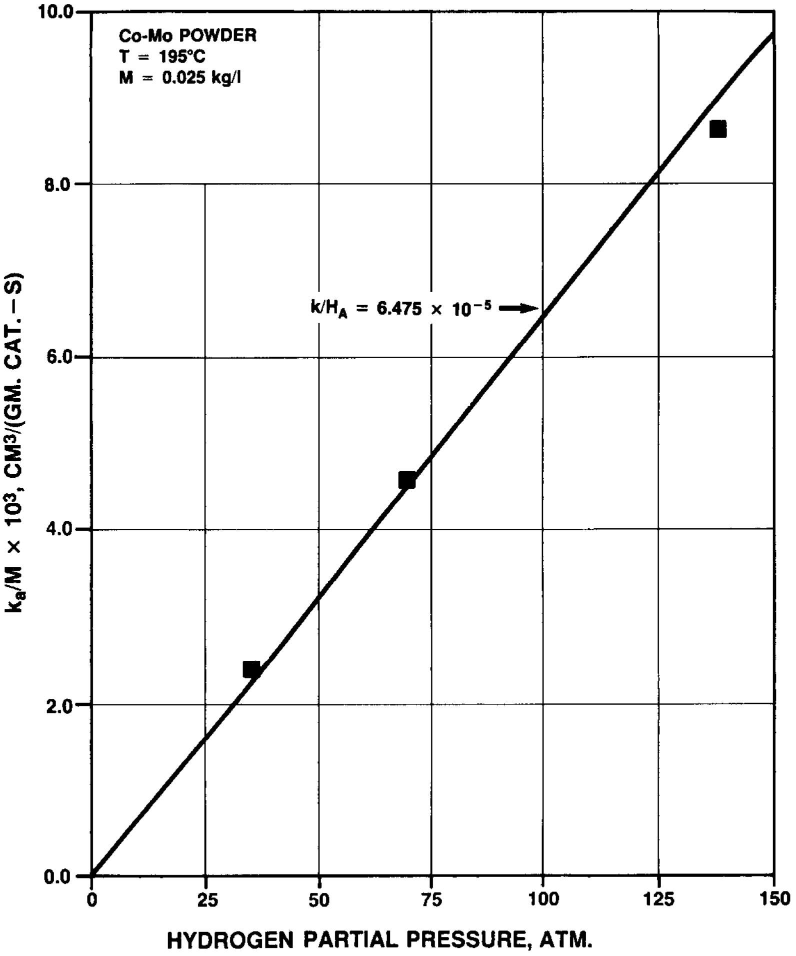


FIG. 3. Pseudo-first-order rate constants as a function of hydrogen partial pressure.

various intrinsic reaction rate expressions is attempted. Justification for the use of Eq. (2) in this work was provided by evaluating the solubility of hydrogen over the entire range of liquid-phase compositions encountered during reaction using various thermodynamic correlating equations for gas solubility such as those of Prausnitz and Shair (*28*), O'Connell (*29*), and Kung *et al.* (*30*). For example, the Prausnitz and Shair (*28*) equation relates the solubility of gaseous reactant A to the liquid mixture composition according to

$$-\ln x_{A,\mathrm{mix}} = \ln(f_A^L/f_A) + v_A^L(\bar{\delta}_s - \delta_A)^2/RT. \quad (6)$$

In this equation, $x_{A,\mathrm{mix}}$ is the mole fraction of hydrogen in the liquid phase, f_A^L is the fugacity of hypothetical liquid hydrogen, f_A is the fugacity of hydrogen at 1 atm pressure, v_A^L is the molar volume of hypothetical liquid hydrogen, and $\bar{\delta}_s$ and δ_A are the solubility parameters for the liquid mixture and hydrogen, respectively. Detailed equations for evaluation of the various parameters on the right-hand side of Eq. (6) are omitted for brevity but are given elsewhere (*20*) along with comparisons between the various other cited correlations and example calculations. At T = 468 K (195°C) corresponding to the data in Fig. 1, one obtains f_A^L = 313.4 atm, v_A^L = 63 cm^3 mol^{-1}, δ_A =

3.17 $(\mathrm{cal/cm^3})^{1/2}$, and $\bar{\delta}_s$ = 6.81 $(\mathrm{cal/cm^3})^{1/2}$ when the MT_2MA conversion $X = 0$. Similarly, $\bar{\delta}_s$ = 6.78 $(\mathrm{cal/cm^3})^{1/2}$ when $X = 50\%$. Substituting these values into Eq. (6) using $f_A = 1$ atm yields $x_{A,\mathrm{mix}} = 1.301 \times 10^{-3}$ at $X = 0$ and $x_{A,\mathrm{mix}} = 1.319 \times 10^{-3}$ at $X = 50$ so that the hydrogen solubility is nearly constant. This result is not surprising since the liquid-phase mole fraction of solvent is greater than 90% and the principle liquid-phase species have a similar chemical structure. Thus, use of Eq. (2) corresponding to a fixed value of Henry's law constant seems justified in this case.

Reaction rate equations for hydrogenation and hydrodesulfurization of thiophenic species such as benzene, biphenyl, naphthalene, and dibenzothiophene were identified by Gates and co-workers (*22–24*) by comparison to batch and flow reactor data. The rate equations that gave the best agreement with experimental results included inhibition due to the liquid reactant, hydrogen sulfide, and hydrogen, but otherwise were first-order with respect to hydrogen and the liquid reactant, respectively. Our results do not indicate any inhibition by the liquid reactant or hydrogen over the given ranges of concentration and pressure, but do exhibit first-order dependent with respect to both the gas and liquid reactants. Inhibition of our observed reaction rates by either hydrogen sulfide or methylmercaptan seem possible for our system, but this could not be detected from various batch reactor data where varying amounts of these were initially present in the liquid feed. The absence of a support material such as γ-Al_2O_3 in our catalyst precursor may be partly responsible for the observed lack of inhibition, but more detailed studies, preferably in a continuous flow reactor, are needed before this assessment can be made.

Hydrodesulfurization of MT_2MA readily occurs at lower temperature with a higher specific reaction rate than thiophenic or related species. For example, evaluation of Eq. (5) at $T = 468$ K, $\bar{p}_A = 137.1$ atm, and $C_B = 3.0 \times 10^{-4}$ mol cm^{-3} yields $r = 2.7 \times 10^{-6}$ mol/g cat.-s. This value for the reaction rate is an order-of-magnitude greater than $r = 1.5 \times 10^{-7}$ mol/g cat.-s at $T = 573$ K and $\bar{p}_{H_2} = 1.8 \times 10^4$ kPa given by Broderick and Gates (*24*) in Fig. 6 of their paper where $C_{H_2S} = 0$ corresponding to the maximum observed value. This result is not surprising since the carbon–sulfur bond in MT_2MA is present in a substituent group on the aromatic ring versus within the aromatic ring itself as typically encountered in the sulfur species present in petroleum fractions.

SUMMARY

Catalytic hydrodesulfurization of *ortho*-aminobenzylsulfides to *ortho*-alkylanilines has been identified as a significant reaction step in the synthesis of certain key chemical intermediates. Application of typical petroleum hydrodesulfurization catalysts to a particular aromatic sulfide with trifluoromethyl as a substituted group has been shown to give unacceptable results, while carbon-supported and unsupported cobalt–molybdenum oxides give high selectivity to the desired product. For the unsupported oxides, it was shown that various unsupported $Co_xMo_yO_z$ catalyst precursors with x/y in the range 1/4 to 4/1 gave high selectivity to the organic product.

The results of an abbreviated reaction kinetic study have shown that the hydrodesulfurization of the *ortho*-aminobenzylsulfide has a reaction rate that exhibits first-order dependence on both the gas and liquid reactants over a limited range of gas pressure and liquid reactant concentration. The reaction rates are an order-of-magnitude greater than those for hydrodesulfurization of typical compounds present in petroleum fractions at corresponding lower reaction temperature.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Mr. Hayat Rahman, W. A. Stultz, and P. T. Chambers with the experimental program. We also wish to acknowledge the assistance of Mr. J. T. Scanlon and Dr.

D. E. Willis in development of the GC analytical method. Dr. T. R. Felthouse provided some useful comments during preparation of the manuscript.

REFERENCES

1. Photaki, I., *in* "Topics in Sulfur Chemistry" (A. Senning, Ed.), Vol. 1. George Thieme, Stuttgart, 1976.
2. Block, E., "Reactions of Organosulfur Compounds." Academic Press, New York, 1978
3. Goldfarb, Y. L., Fabrichnyi, B. P., and Shalavina, I. F., *Tetrahedron* **18,** 21 (1962).
4. Meyers, A. I., "Heterocycles in Organic Synthesis." Wiley, New York, 1974.
5. Farnier, M., Soth, S., and Fournari, P., *Canad. J. Chem.* **54,** 1083 (1976).
6. Miyahara, Y., Inazu, T., and Yoshino, T., *Chem. Lett.* 563 (1978).
7. Shulman, S. C., and Shalit, H., *Catal. Rev.-Sci. Eng.* **4,** 245 (1970).
8. Schuit, G. C. A., and Gates, B. C., *AIChE J.* **19,** 417 (1973).
9. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," Chap. 5. McGraw–Hill, New York, 1979.
10. Bonner, W. A., and Gromm, R. A., *in* "The Chemistry of Organic Sulfur Compounds" (N. Kharasch and C. Y. Meyers, eds.), Vol. 2, pp. 35–71.
11. Pettit, G. R., and van Tamelen, E. E., *Org. React. (N.Y.)* **12,** 356 (1962).
12. Hauptmann, H., and Walter, W. F., *Chem. Rev.* **63,** 347 (1962).
13. Badger, G. M., Kowanko, N., and Sasse, W. H. F., *J. Chem. Soc.*, 440 (1959).
14. Grange, P., *Catal. Rev.-Sci. Eng.* **21,** 135 (1980).
15. Weisser, O., and Landa, S., "Sulphide Catalysts, Their Properties and Applications," pp. 210–244. Pergamon, New York, 1973.
16. Mozingo, R., Spencer, C., and Kolkers, K., *J. Amer. Chem. Soc.* **66,** 1859 (1944).
17. Djerassi, C., and Williams, D. H., *J. Chem. Soc.*, 4046 (1963).
18. Torrey, S., Ed., "Preemergence Herbicides." Noyes Data Corp., Park Ridge, N.J., 1982.
19. U.S. Patent 2,793,984.
20. Mills, P. L., and Tremont, S. J., in preparation.
21. Claus, P., and Vycudilik, W., *Tetrahedron Lett.* **32,** 3607 (1968).
22. Sapre, A., and Gates, B. C., *Ind. Eng. Chem. Proc. Des. Dev.* **21,** 86 (1982).
23. Broderick, D.H., Sapre, A. V., Gates, B. C., Kwart, H., and Schuit, G. C. A., *J. Catal.* **73,** 45 (1982).
24. Broderick, D. H., and Gates, B. C., *AIChE J.* **27**(4), 663 (1981).
25. Lemcoff, N. O., *J. Catal.* **46,** 346 (1977).
26. Komiyama, H., and Smith, J. M., *AIChE J.* **21,** 664 (1975).
27. Satterfield, C. N., Ma, Y. A., and Sherwood, T. K., *Inst. Chem. Eng. Symp. Ser.*, 28 (1968).
28. Prausnitz, J. M., and Shair, F. H., *AIChE J.* **7**(4), 682 (1961).
29. O'Connell, J. P., *AIChE J.* **17**(3), 658 (1971).
30. Kung, J. K., Nazario, F. N., Joffe, J., and Tassios, D., *Ind. Eng. Chem. Proc. Des. Dev.* **23**(1), 170 (1984).

S. J. TREMONT
P. L. MILLS[1]

Monsanto Company
Central Research Laboratory
800 N. Lindbergh Blvd.
St. Louis, Missouri 63167

Received February 27, 1985

---

[1] To whom correspondence should be sent.