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A novel methodology towards deep desulfurization of light oil effected by sulfimides formation

Yasuhiro Shiraishi, Tomoko Naito, Takayuki Hirai* and Isao Komasawa

Department of Chemical Science and Engineering, Graduate School of Engineering Science, and
Research Center for Solar Energy Chemistry, Osaka University, Toyonaka 560-8531, Japan.
E-mail: hirai@cheng.es.osaka-u.ac.jp

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A novel desulfurization process for light oil, based on *N*-tosylsulfimide formation by the reaction of sulfur compounds with chloramine T (sodium *N*-chlorotoluene-*p*-sulfonamide), has enabled deep desulfurization at ambient temperature.

Much attention has been focused on the deep desulfurization of light oil, since the sulfur oxy-acids (SOx) contained in diesel exhaust gas cause air pollution and acid rain. The sulfur level in diesel fuels is limited presently to 0.05 wt%, both in Japan and Europe. The current technology of hydrodesulfurization (HDS) can desulfurize aliphatic and acyclic sulfur-containing compounds quite adequately, when adopted on the industrial scale. The above process however is limited, when treating dibenzothiophene (DBT), especially DBTs having alkyl substituents on their 4 and/or 6-position.[1] Thus, the production of light oil, of very low level sulfur, inevitably requires severe high energy conditions and specially active catalysts. In the development of any alternative energy-efficient desulfurization process, a radical approach, which is not limited to conventional HDS technology, is required.

Various kinds of sulfur-containing compounds have been reported to react with chloramine T, in hydrogen-donating solvents such as alcohol and water, to give rise at ambient temperature to crystalline powders of the corresponding *N*-tosylsulfimides.[2–5] These sulfimides are highly polarized and are insoluble in nonpolar hydrocarbon solvents. Thus, such a synthetic method, if applied to the desulfurization of nonpolar light oil, might thus be able to remove the DBTs specifically from the light oil under moderate conditions.

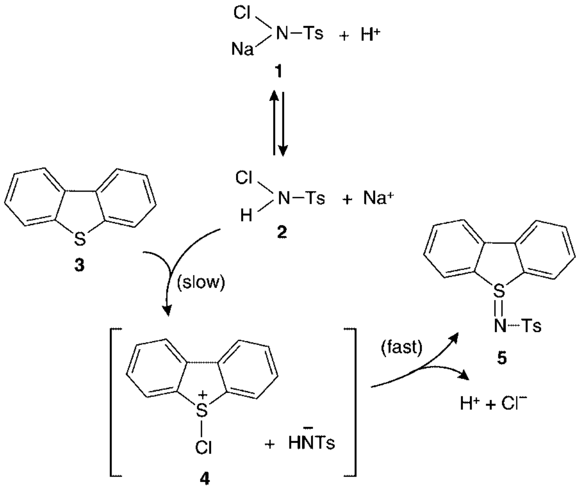
In order to test the feasibility of this idea, a *n*-tetradecane solution (50 ml) containing DBT (11 mmol l^{-1}), corresponding to a sulfur content of 0.05 wt%, was used as a model light oil. An alcohol solution (10 ml), to which a required amount of chloramine T trihydrate was dissolved, was then added to the above tetradecane solution at 323 K. In this procedure, the removal efficiency for DBT from tetradecane, following 3 h of reaction, was however only 5%, as shown in Table 1 (entry 1). As reported[6] and shown in Scheme 1, the sulfimide **5** is formed *via* the chlorination of the sulfur atom for **3** by the free-state chloramine T **2**, produced by the hydrolysis of **1**. The rate of the chlorination is therefore accelerated with decreasing pH of the solution, owing to the acceleration of the hydrolysis of **1**. The desulfurization of DBT, when a small amount of AcOH was added into the reaction mixture, was accelerated significantly (entry 2). The addition of the AcOH improves the desulfurization when used with MeOH, but is ineffective when used with the other solvents such as EtOH and *i*-PrOH (entries 3 and 4). This is because the hydrogen-donation ability of the latter two solvents is lower than that of MeOH. The desulfurization of DBT was also accelerated with increasing the concentrations of chloramine T and AcOH (entries 5–7). Both MeOH and chloramine T are insoluble in the nonpolar tetradecane, such that the resulting tetradecane is recovered easily using a separation funnel. When an equal volume of water to that of MeOH was added into the resulting MeOH solution, the *N*-tosylsulfimide of the DBT precipitated on the bottom of the flask, thus suggesting that the sulfimide formed is removed successively into the MeOH solution during the reaction.

Table 1 Desulfurization yield of DBT from tetradecane following the reaction with chloramine T under differing conditions[a]

Entry	Alcohol	AcOH/ml	Chloramine T/mmol	Desulfurization (%)
1	MeOH	–	1.1	5.0
2	MeOH	1	1.1	70.6
3	EtOH	1	1.1	1.5
4	*i*-PrOH	1	1.1	6.7
5	MeOH	1	5.5	98.5
6	MeOH	1	2.75	95.2
7	MeOH	2	1.1	> 99.9

[a] Temperature: 323 K, time: 3 h, tetradecane volume: 50 ml, alcohol volume: 10 ml, initial DBT content in tetradecane: 11 mmol l^{-1} (0.55 mmol).

The above procedure was then tested for the desulfurization of methyl-substituted DBTs, which are key compounds in the HDS technology.[1] In the present process, as shown in Fig. 1, the desulfurization rates for 4-methyl- and 4,6-dimethyl-DBT from tetradecane were higher than that of nonsubstituted DBT. This tendency differs completely from that obtained by the HDS method.[1] As shown in Scheme 1, the rate-determining step for the present reaction is the chlorination of the nucleophilic sulfur atom for the DBT **3** by **2**. Semiempirical MO calculation[7] showed that the electron density on the sulfur atom for DBTs lies in the order 4,6-dimethyl (5.7597) > 4-methyl (5.7586) > DBT (5.7577), which agrees well with the actual desulfurization reactivity (Fig. 1). The result suggests that the rate of the chlorination depends on the electron density (nucleophilicity) on the sulfur atom for DBTs, and as a result, methyl-substituted



Scheme 1 Formation of DBT sulfimide by chloramine T.

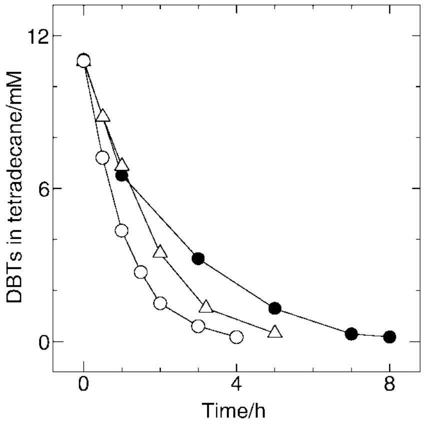


Fig. 1 Time-course variation in the concentration of (●) DBT, (△) 4-methyl-DBT and (○) 4,6-dimethyl-DBT in tetradecane. Temperature: 323 K, tetradecane volume: 50 ml, MeOH volume: 10 ml, AcOH volume: 1 ml, initial DBTs content in tetradecane: 11 mmol l^{-1} (0.55 mmol).

DBTs, having high electron density are desulfurized more easily than the nonsubstituted DBT.

The above process was then applied to the desulfurization of actual light oil containing *ca.* 0.19 wt% sulfur (2.47 mmol), which is just below the previous regulatory value that used to apply in Japan (0.2 wt%). The MeOH solution (50 ml) containing various amount of chloramine T was then added to the light oil (50 ml) in the presence of 2 ml AcOH, and was stirred at 323 K. Upon addition of water to the resulting MeOH solution, a yellow–white solid precipitate adhered to the bottom of the flask. As shown in Fig. 2b, the IR spectrum for the precipitate demonstrated two intense absorption bands at 1180 and 1300 cm^{-1} owing to the sulfonyl group and also a small band at 980 cm^{-1} owing to the S–N bond for the sulfimides. The spectrum is similar to that for *N*-tosylsulfimide of DBT (Fig. 2a), thus indicating that the sulfimides, formed during the reaction, are removed successfully from the light oil into the MeOH solution. As shown in Table 2, the sulfur content of the light oil decreased with increasing the chloramine T concentration. However, the deep desulfurization (0.05 wt%) was hardly achieved, even in the presence of 10-fold molar excess of chloramine T based on the initial sulfur concentration of the feed light oil (entry 3). The desulfurization yields obtained are significantly smaller than those expected from the data for the model light oil, as shown in Fig. 1.

The actual light oil contains a large amount of DBTs, with several types of hydrophobic alkyl substituents on the molecule, and the polarity of the DBTs is decreased with increasing the carbon number of the substituents.[8] The low desulfurization efficiency of the light oil is thus probably because the low polarity sulfimides of DBTs having large carbon number of substituents, formed by the reaction with chloramine T, are not removed into the MeOH solution but remain in the resulting light oil. Since the sulfimides have a higher polarity as compared to the other constituents of the light oil, they might be removed by the addition of solid adsorbents, such as aluminum oxide and silica gel. As shown in Table 2 (entry 2b), the sulfur concentration of light oil was actually decreased by the addition of the adsorbents, with the deep desulfurization (0.05 wt%) being achieved successfully. As shown in Fig. 2c, the adsorbed materials showed absorption bands owing to the sulfonyl group and the S–N bond for sulfimides as also found for the spectrum of the precipitate (Fig. 2b). The spectrum for the adsorbed material also showed a larger absorption band at 1620 cm^{-1}, owing to the alkyl group, as compared to that obtained for the precipitate, indicating that the sulfimides of the DBTs, having a large carbon number of alkyl substituents, are adsorbed successfully.

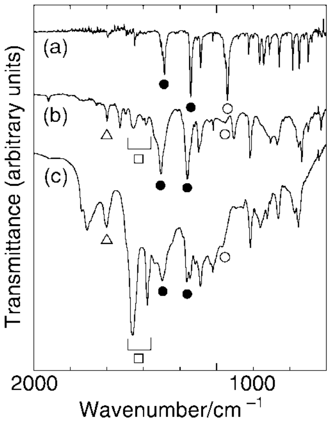


Fig. 2 IR spectra for (a) *N*-tosylsulfimide of DBT, (b) precipitate obtained by the addition of water to the MeOH solution following the reaction of light oil with chloramine T, and (c) adsorbed material obtained by the addition of silica gel to the light oil following the reaction with chloramine T. (○) S–N bond, (●) sulfonyl group, (□) aliphatic hydrogen (C–H) and (△) aromatic hydrogen (C–H).

Table 2 Variations in the sulfur content of light oil following (a) reaction with chloramine T and (b) subsequent addition of adsorbents[a]

	(a)		(b)	
Entry	Chloramine T/mmol	Sulfur content/wt%	Adsorbent/g ml^{-1}-oil	Sulfur content/wt%
1	4.65	0.099	—	—
2	11.6	0.079	0.2 (Al_2O_3) 0.2 (SiO_2) 0.3 (SiO_2)	0.054 0.050 0.048
3	23.3	0.066	—	—

[a] Temperature: 323 K, time: 10 h, light oil volume: 50 ml, MeOH volume: 50 ml, AcOH volume: 2 mL, initial sulfur content of light oil: 0.190 wt% (2.47 mmol).

The present study describes a novel desulfurization process for light oil, based on the removal of *N*-tosylsulfimides produced by the reaction of sulfur compounds with chloramine T. The deep desulfurization was achieved successfully at ambient temperature. The refractory DBTs in the current HDS process are desulfurized easily by the present process, thus showing that the present process is both energy-saving and effective as a new deep desulfurization process for light oil. The sulfimides have been reported to have antimicrobial, diuretic and hypotensive properties on tumor growth and activity as antidepressants and stimulants of the central nervous system.[5] It may thus be interesting to use the recovered sulfimides from the desulfurization process, as novel materials for medicinal supplies.

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Notes and references

1 M. Houalla, D. H. Broderick, A. V. Sapre, N. K. Nag, V. H. J. De Beer, B. C. Gates and H. Kwart, *J. Catal.*, 1980, **61**, 523.
2 B. H. Nicolet and J. Willard, *Science*, 1921, **53**, 217.
3 F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1922, **121**, 1052.
4 T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, 1977, **77**, 409.
5 B. M. Tros and L. S. Melvin, Jr., *Sulfur Ylides*, Academic Press, New York, 1975.
6 K. Tsujihara, N. Furukawa, K. Oae and S. Oae, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2631.
7 The theoretical calculations of the electron density on sulfur atom for DBTs were performed with the PM3 semiempirical method within the WinMOPAC ver 2.0 software (Fujitsu, Inc).
8 Y. Shiraishi, Y. Taki, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.*, 2001, **40**, 1213.