CHEMISTRY LETTERS, pp. 535 - 538, 1984.

HIGH EFFICACY OF ULTRASONIC-PROMOTED REDUCTIVE ALKYLATION OF COAL

Mikio MIYAKE,* Ryōichi UEMATSU, and Masakatsu NOMURA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, 2-1, Yamada-oka, Suita, Osaka 565

Yūbari coal is efficiently anionized by sodium metal in hexamethylphosphoric triamide (HMPA) under ultrasonic irradiation at ambient temperature. An ethylated coal prepared from the anionized coal and ethyl iodide shows 90 wt% of solubility in benzene. The improved method solves problems of the conventional Sternberg method of reductive alkylation of coal.

In spite of the recent progress in solid-state spectroscopy, coal derivatives soluble in organic solvents still give more detailed information about coal structure than analysis of solid coal directly. To get such soluble derivatives, a mild chemical reaction is preferred to prevent destruction of macromolecular structure of original coal. However, a large portion of organic matter in coal needs to be solubilized. The reductive alkylation method proposed by Sternberg et al.[1)] is accepted to be one of the most excellent methods to satisfy the above requirements, because a large portion of bituminous coal can be solubilized in benzene under mild reaction conditions at room temperature.[1-4)] The method consists of coal anion formation reaction by potassium metal in tetrahydrofuran (THF) containing naphthalene, as an electron transfer agent, and subsequent alkylation of the formed "coal anion" by alkyl iodide.[1-4)] However, the Sternberg procedure contains some problems, such as long reaction time of 2-14 days,[1-4)] contamination of products by naphthalene,[5)] and employment of potassium metal with quite high chemical activity (inferior results have been reported with sodium and lithium metals.[1,4)]) Although several alternative methods have been proposed,[6-8)] no method satisfactorily solves these problems. The authors have reported [9,10)] an improved method which solves the first two problems, by conducting coal anion formation reaction in refluxing THF (bp 66 °C) with molten potassium metal (mp 63 °C) and without naphthalene. However, this method is not applicable to sodium and lithium systems, since these metals remain solid state at THF refluxing temperature.

We now wish to report here another improved method which solves all the problems described above by conducting reaction under ultrasonic irradiation in HMPA. Ultrasonic-promoted reactions have been become of much interest in recent years; striking effects in the synthetic organic reactions have been reported.[11-14)] Ultrasonic energy has also been applied to coal-extraction procedures.[15-18)] However, no report has yet appeared about benefical effect of ultrasonic irradiation in reactions of coal.

Reactions were carried out in a three-necked flask (100 cm^3) containing solvent (50 cm^3) and metallic sodium cuts (2 g) under a dry argon stream. The solvent used was THF, 1,2-dimethoxyethane (DME), or HMPA. In some cases, 0.15 g of naphthalene was added as an electron transfer agent. The flask was previously irradiated in a water bath of a Bransonic B-220 ultrasonic cleaner (100 W, 45 kHz) for about 20 min, and the solution turned to characteristic deep green colour. Then, 3 g of ground Yūbari coal (-200 U.S. mesh), dried at 90 °C under vacuum for 12 h, was added to the flask which was irradiated further for prescribed time (0.5-6 h, usually 6 h) to prepare "coal anion" at ambient temperature. The temperature of the water bath was below 45 °C. Next, the flask was transferred on a magnetic stirrer and ethyl iodide (100 g) was added dropwise over 30 min period at about 10 °C. The mixture was further stirred for overnight at room temperature to ethylate the "coal anion". After the reaction, the mixture was evacuated by using rotary vacuum evaporaters, and washed with acidified water with dilute hydrochloric acid at first and subsequently with de-ionized water repeatedly (more than 10 times) until no halogen ion was detected in the filtrate. The solid product recovered after drying to constant weight at 90 °C under vacuum for 12 h was termed ethylated coal. Two grams of the ethylated coal was subjected to Soxhlet extraction with benzene. Detailed procedures, such as purification of the solvents, recovery of the products, and analytical methods were previously described.[9,10] Values of solubility and ultimate analysis of ethylated coals were estimated on dry-ash-free basis whereas those of recovery were on dry basis.

Properties of ethylated coals prepared in various solvents under ultrasonic irradiation for 6 h are shown in Table 1, which contains the items: recovery and solubility of ethylated coals and number of ethyl groups introduced per 100 carbon atoms estimated by three kinds of methods. When the reaction was carried out in THF containing naphthalene, similar solvent to the Sternberg method, the resulted ethylated coal contains 4.0-7.1 ethyl groups per 100 carbon atoms, giving 58 wt% of soluble product in benzene. These values are comparable to those reported by the conventional procedure; for example, 5.5 methyl groups per 100 carbon atoms and 61 wt% of solubility of methylated Yūbari coal prepared by 48 h of reaction with potassium metal.[3] Therefore, the reaction time is effectively reduced irrespective of the use of sodium metal. Such result is compatible with the report that ultrasonic irradiation has promoted the formation of naphthalene anion radical with sodium in THF.[12]

Table 1. Properties of ethylated coals prepared in various solvents[a]

Solvent	Recovery/ wt%	Solubility in benzene/ wt%	No. of Et/100 C		
			A.R.[d]	C.B.[e]	M.B.[f]
THF[b]	113	58	4.0	7.1	6.7
DME	109	60	4.9	6.0	4.9
DME[b]	118	68	6.0	9.5	9.1
HMPA	118	90	7.1	8.4	9.1
THF[c]	118	86	8.9	9.6	9.3

a) Reacted with Na for 6 h. b) Naphthalene (0.15 g) was added as an electron transfer agent. c) Yūbari coal (10 g) was subjected to the reaction with molten K (4 g) under refluxing THF. d) From H/C atomic ratios. e) Carbon balance. f) Material balance.

DME is known to have more capacity for the solvation of alkali metal than THF.[4] Therefore, the reaction was conducted in DME in place of THF. The extent of the alkylation reaction and the conversion to soluble product are comparable in DME without an electron transer agent to that in THF with an electron transfer agent (Table 1). Presence of naphthalene in DME slightly enhances the reaction. Thus DME is superiour solvent to THF. The solvent systems containing naphthalene showed higher values of recovery than those without naphthalene. In addition, numbers of ethyl groups estimated by three kinds of methods differed considerably for the former systems; the values estimated by carbon balance and material balance are higher than those by H/C atomic ratios. These results suggest that the ethylated products from the solvent systems containing naphthalene are contaminated by naphthalene, similarly to the conventional products.5) Accordingly the use of naphthalene is unfavorable.

Table 2. Properties of ethylated coals prepared in HMPA

Reaction time/h	Recovery/ wt%	Solubility in benzene/ wt%	No. of Et/100 C a)		
			A.R.	C.B.	M.B.
Original coal		2	–	–	–
0.5	110	43	3.9	5.8	5.1
2	113	64	5.1	6.5	6.6
6	118	90	7.1	8.4	9.1
6 b)	98	6	–	–	–
6 c)	98	10	–	–	–

a) Notations are the same as in Table 1.
b) Reacted in the absence of Na.
c) Reacted in the ultrasonic bath without irradiation. The flask was shaken occasionally.

Table 3. Ultimate analyses and number of HMPA molecules in ethylated coals

Reaction time/h	Ultimate analysis				No. of HMPA/ 100 C	
	C	H	N	O a)	A.R. b)	N.B. c)
– d)	86.0	6.2	2.3	5.5	–	–
0.5	86.8	7.1	2.2	3.9	0.02	0.04
2	85.4	7.3	2.3	5.0	0.09	0.09
6	84.6	7.6	2.4	5.4	0.20	0.17

a) Difference. b) From N/C atomic ratios. c) Nitrogen balance. d) Original coal.

Then, the reaction in HMPA is examined, which forms more stable blue solutions with alkali metals than any ethereal solvents. An effective reaction is expected in HMPA even in the absence of an electron transfer agent. As can be seen in Table 1, quite excellent results are obtained in HMPA without naphthalene; the product contains 7.1-9.1 ethyl groups, which shows 90 wt% of solubility in benzene. The attained values are comparable to those of ethylated Yūbari coal prepared by previously proposed improved method9,10) in refluxing THF with molten potassium metal (Table 1). It should be emphasized that present method uses sodium metal with relatively low chemical activity at ambient temperature with the aid of ultrasonic energy.

Reactions in HMPA were carried out by changing the reaction time to estimate the extent of the reaction at an early stage (Table 2). The solubility of original Yūbari coal in benzene is only 2 wt%. However, when the coal was treated with sodium metal for only 0.5 h followed by ethylation, 3.9-5.8 ethyl groups were introduced in the product which showed 43 wt% of solubility in benzene. The extent of the conversion of the coal to ethylated products clearly depends on the reaction time, as a similar manner to the improved method with molten potassium in refluxing THF.9,10) When the coal was allowed to react in the absence of sodium metal in HMPA under ultrasonic irradiation for 6 h, the solubility of the product remains negligibly small extent (Table 2). This result suggests that little ultrasonic energy destructs coal structure to bring soluble products. On the other hand, without ultrasonic irradiation, the reaction also proceeds to only a small extent (Table 2). Thus ultrasonic energy is necessary to achieve such effective reaction. One of the important roles of ultrasonic energy is reported12) to keep the metal surface free from contaminative species.

Ultimate analyses of original coal and ethylated products prepared in HMPA by changing reaction time are summarized in Table 3. An increase in H% depending on extension of the reaction time is responsible to amount of ethyl groups introduced whereas some products show rather high N and O%. Such high oxygen content may be ascribed to chemisorption of oxygen during processing, as reported for the conventional products.2,9,10) On the other hand, there is a possibility that the high N content is due to contamination of HMPA in ethylated products. Therefore, number of HMPA molecules per 100 carbon atoms is estimated by two kinds of methods (Table 3). All the values obtained are lower than the corresponding number of ethyl groups shown in Table 2.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 57750729).

References

1) H. W. Sternberg, C. L. Delle Donne, P. Pantages, E. C. Moroni, and R. E. Markby, Fuel, 50, 432 (1971).
2) H. Wachowska, Fuel, 58, 99 (1979).
3) T. Kato, S. Hashimoto, and H. Tsukashima, Nenryo Kyokai Shi, 60, 426 (1981).
4) L. B. Alemany and L. M. Stock, Fuel, 61, 250 (1982).
5) J. A. Franz and W. E. Skiens, Fuel, 57, 502 (1978).
6) L. Lazarov, I. Rashkov, and S. Angelov, Fuel, 57, 637 (1978).
7) B. Ignasiak, D. Carson, and M. Gawlak, Fuel, 58, 833 (1979).
8) C. I. Handy and L. M. Stock, Fuel, 61, 700 (1982).
9) M. Miyake, M. Sukigara, M. Nomura, and S. Kikkawa, Fuel, 59, 637 (1980).
10) S. Kikkawa, M. Miyake, M. Sukigara, and M. Nomura, Nippon Kagaku Kaishi, 1980, 939.
11) B. H. Han and P. Boudjouk, J. Org. Chem., 47, 5030 (1982).
12) T. Azuma, S. Yanagida, H. Sakurai, S. Sasa, and K. Yoshino, Synth. Commun., 12, 137 (1982).
13) T. Kitazume and N. Ishikawa, Chem. Lett., 1982, 1453.
14) J. L. Luche, C. Petrier, J. P. Lansard, and A. E. Greene, J. Org. Chem., 48, 3837 (1983).
15) L. L. Anderson, M. Y. Shifai, and G. R. Hill, Fuel, 53, 32 (1974).
16) H. Tsuboi, K. Nagoya, M. Nagai, M. Nakano, and M. Kasagi, Nenryo Kyokai Shi, 57, 918 (1978).
17) N. E. Cooke and R. P. Gaikwad, Can. J. Chem. Eng., 61, 697 (1983).
18) W. R. Jackson, F. P. Larkins, P. Thewlis, and L. Watkins, Fuel, 62, 606 (1983).

(Received January 17, 1984)