A Facile Desulfurization Reaction with a Combination of Two Kinds of Metals in Acidic Media. The Synthesis of Hypoxanthine

Nobuhiro Nakamizo*, Kazuo Shiozaki, Seiichi Hirai, and Shiro Kudo
Sakai Factory, Kyowa Hakko Kogyo Co., Ltd., Sakai, Osaka

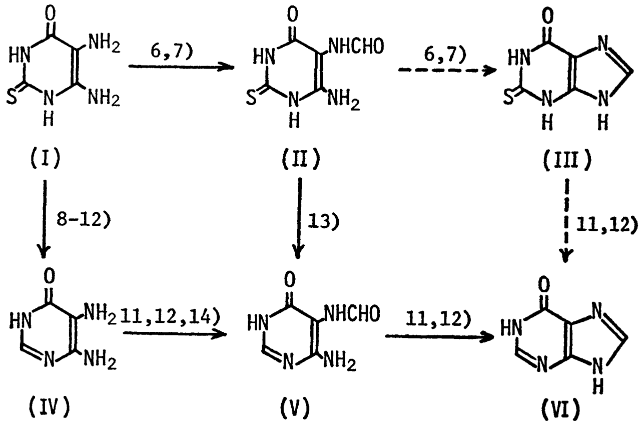
(Received February 15, 1971)

A facile desulfurization procedure has been presented for the method that synthesizes hypoxanthine in one step by heating 4,5-diamino-6-hydroxy-2-mercaptopyrimidine with a desulfurizing agent in formic acid. When Raney nickel prepared in the usual way was used as the desulfurizing agent, it was necessary for the ratio of nickel atoms to sulfur atoms (the Ni/S ratio) to be more than 2.6 : 1. On the contrary, when the Raney alloy *per se* was used, the amount of nickel could be diminished to a catalytic amount (Ni/S 0.2—0.3). The higher the content of aluminum in the alloy, the smaller the Ni/S ratio required for the desulfurization. In contrast with usual desulfurization reactions carried out in neutral media, most of the sulfur was released from the reaction mixture as hydrogen sulfide. Although aluminum or iron powder by itself had little desulfurizing activity, its addition to the Raney alloy was useful in diminishing the Ni/S ratio. Furthermore, combinations of nickel or cobalt salts and aluminum or iron powder were as effective as the Raney alloy as desulfurizing catalysts. In the case of a combination of nickel formate and aluminum powder, a large portion of the nickel ion was proved to be reduced to metallic nickel. The desulfurization reaction also proceeded smoothly in an aqueous solution of hydrochloric or sulfuric acid. On the basis of these facts, a mechanism was proposed with which the active nickel catalyst is regenerated by such auxiliary metals as aluminum or iron.

Since the study[1] by Bougault *et al.* in 1939, desulfurization reactions of sulfur-containing organic compounds by means of Raney nickel have been extensively used both for synthesis and for structure determination.[2-4] In general, the desulfurization reactions are conducted by heating a mixture of sulfur-containing substrates with "excess" Raney nickel (the ratio of Ni : substrate by weight being from about 1 : 1 to 10 : 1) in such a solvent as ethanol. The hydrogen required for the formation of a new C–H bond usually comes, not from external hydrogen, but from that retained by the catalyst during its preparation. Most of the original sulfur is converted to nickel sulfide during desulfurization.[5]

From such characteristics of the reaction, it can be said that it is undesirable for reductive desulfurization to use an amount of Raney nickel less than that required for the formation of nickel sulfide. In practice, much more of the catalyst than the theoretical amount must be used in order to obtain a good yield. From an industrial standpoint, however, not only Raney nickel is expensive, but also its preparation on a large scale is very troublesome. Consequently, in spite of the usefulness of this procedure in laboratory work, its industrial application has been highly limited.

In the synthesis of hypoxanthine (VI) from 4,5-diamino-6-hydroxy-2-mercaptopyrimidine (I) (Scheme 1), the present authors found that, when the desulfurization is carried out with the Raney nickel *alloy* itself or with a combination of a nickel salt and aluminum (or iron) powder in an acidic medium, it is possible to decrease the amount of nickel required to a great extent.



Scheme 1

Experimental

Materials. The formic acid, sodium dithionite, metallic salts, and metallic powder were all of commercial

---

* Present address: Tokyo Research Laboratory, Kyowa Hakko Kogyo Co., Ltd., Asahi-machi, Machida-shi, Tokyo.

[1] J. Bougault, E. Cattelain, and P. Chabrier, *Compt. Rend.*, **208**, 657 (1939).

[2] G. R. Pettit and E. E. van Tamelen, "Organic Reactions," Vol. 12, p. 356 (1962).

[3] H. Hauptmann and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962).

[4] W. A. Bonner and R. A. Grimm, "The Chemistry of Organic Sulfur Compounds," ed. by N. Kharasch and C. Y. Meyers, Vol. 2, Pergamon Press, London (1966), p. 35.

[5] L. Granarelli, *Anal. Chem.*, **31**, 434 (1959).

[6] W. Traube, *Ann. Chem.*, **331**, 64 (1904).

[7] G. B. Elion, W. H. Lange, and G. H. Hitchings, *J. Amer. Chem. Soc.*, **78**, 217 (1956).

[8] R. O. Roblin, J. O. Lampen, J. P. English, Q. P. Cole, and J. R. Vaughan, *ibid.*, **67**, 290 (1945).

[9] H. Getler, P. M. Roll, J. F. Tinker, and G. B. Brown, *J. Biol. Chem.*, **178**, 259 (1949).

[10] A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, **1951**, 474.

[11] G. B. Elion, E. Burgi, and G. H. Hitchings, *J. Amer. Chem. Soc.*, **74**, 411 (1952).

[12] Y. Mizuno, T. Ueda, M. Kobayashi, Y. Shimizu and T. Murakami, *Yakugaku Zasshi*, **77**, 686 (1957).

[13] G. B. Elion, *J. Org. Chem.*, **27**, 2478 (1962).

[14] L. F. Cavalieri and A. Bendich, *J. Amer. Chem. Soc.*, **72**, 2587 (1950).

origin. The Raney nickel alloy was purchased from the Nikki Kagaku Co., Ltd.

4,5-Diamino-6-hydroxy-2-mercaptopyrimidine (I) was prepared by the procedure of Albert *et al.*[10] with some modifications. Into a suspension of 192 g of 4-amino-6-hydroxy-2-mercapto-5-nitrosopyrimidine[6] in 950 m*l* of water, 576 g of sodium dithionite was added with stirring. Within 3 min, the color of the reaction mixture disappeared, the temperature rose from 28°C to 50°C, and the pH dropped from 7 to 5.5. After cooling to 0°C, the product was separated by filtration, washed with water, and dried *in vacuo*. Yield, 99%. (Found: C, 30.69; H, 4.01; N, 35.27; S, 20.41%)

Desulfurization Procedure. In a 3-*l* three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a thermometer, 50.0 g (0.316 mol) of I and 1900 g of formic acid of the concentration desired were placed. After an appropriate amount of the desulfurizing catalyst had then been added, the mixture was refluxed with stirring for eight hours. The gas evolved from the reaction mixture was passed into a 2.5 N solution (1 *l*) of sodium hydroxide in order to collect the hytrogen sulfide, and was finally led to a gas meter. Aliquots of the hydrogen sulfide solution were withdrawn at suitable intervals and analyzed by iodometry. After 8 hr, the waste catalyst was filtered off and washed with formic acid of a concentration equal to that used in the reaction. (Although an evolution of heat from the waste catalyst was sometimes observed during the filtration, there was no danger of ignition.) The filtrate and the washings were then combined and evaporated to dryness under a pressure of 100 mmHg on a water bath. To the residue was added 300 m*l* of water. The crude crystals of hypoxanthine thus obtained were thoroughly triturated, filtered, and washed with 100 m*l* of water.

Analytical Procedure. *Total sulfur* was analyzed by the method of Bethge.[15] *Sulfide-type sulfur* in the waste catalyst was transformed to hydrogen sulfide with hydrochloric acid and determined iodometrically. *Nickel or aluminum* was determined in the form of perchlorate by chelatometric titration. A mixture of an aliquot of the sample dissolved in perchloric acid and 50 m*l* of F/100 EDTA was heated to boiling, and then titrated with F/100 $Pb(NO_3)_2$ at pH 5, using xylenol orange as an indicator, in order to determine the total amounts of Ni and Al.

After this titration, 10 m*l* of a 5% NH_4F solution was added and the mixture was again boiled in order to decompose the Al-EDTA chelate. The EDTA liberated by this treatment was titrated with F/100 $Pb(NO_3)_2$ in order to estimate the amount of Al. From the difference between these two values, the amount of Ni was determined. For samples which contain so little amount Ni or Al that the chelatometric titration could not be used, spectrophotometric analysis[16,17] was applied. If pyrimidines and/or purines were present in the sample, they were decomposed with a nitric acid-perchloric acid mixture before analysing the metals. The amount of metallic nickel in the waste catalyst was determined by subtracting the sum of the amounts of the water-soluble and the sulfide-type nickel from that of the total nickel. Similarly, the amount of metallic aluminum was estimated from the difference between the amount of the water-soluble aluminum and the total aluminum.

Results and Discussion

The Raney-nickel desulfurization reaction is very useful for syntheses of organic compounds, in particular, that of heterocyclic compounds.[2,3] For example, hypoxanthine can be synthesized from 4,5-diamino-6-hydroxy-2-mercaptopyrimidine (I) *via* Raney-nickel desulfurization,[8–12] formylation,[14] and cyclization,[11,12] as is indicated in Scheme 1.

In the procedure to synthesize hypoxanthine in one step by heating the pyrimidine (I) with Raney nickel in 90% formic acid[18], when the ratio of nickel atoms to sulfur atoms (Ni/S ratio) was 6.6 : 1, crude hypoxanthine was obtained in an 87% yield (Table 1). The sulfur content of the product was 0.23%, indicating that the desulfurization was almost complete. The crude product gave pure hypoxanthine in an 83% yield after recrystallization. However, at a Ni/S ratio of less than 2.6 : 1, the reaction was incomplete and gave a deep yellow product which was difficult to purify. Thus, it was confirmed that, so long as Raney nickel is used as a desulfurizing agent, the use of an "excess" of nickel is essential.

TABLE 1. DESULFURIZATION REACTIONS OF I WITH RANEY Ni AND RANEY ALLOY IN 90% FORMIC ACID

Desulfurizing agents	Ni/S	Crude VI yield, %	Sulfur[a] in crude VI %
Raney Ni	6.6	87	0.23
	2.6	79	2.37
	1.8	77	2.73
Ni–Al alloy	2.6	88	0.00
	1.8	78	0.01
	1.3	82	0.00
	1.2	83	0.10
	1.0	76	0.25
	0.8	74	0.08

a) S% for 2-mercapto-6-hydroxypyrimidine: 19.06%.

It is known that the results of the reductive desulfurization depend on the quantity of hydrogen available as well as on that of nickel, as Eqs. (1) and (2) show:

$$\text{R-S-R}' \xrightarrow{\text{Ni}} \text{R}\cdot + \cdot\text{R}' \begin{array}{l} \xrightarrow{\text{excess H}} \text{RH} + \text{R}'\text{H} \qquad (1) \\ \xrightarrow{\text{deficient H}} \text{RR} + \text{RR}' + \text{R}'\text{R}' \qquad (2) \end{array}$$

When a so-called "degassed" catalyst is used, dimeric products are mainly produced.[2,3] For the purpose of the hydrogenolytic desulfurization, as in the present work, the more hydrogen there is, the better will be the result. Papa *et al.*[19] found that nickel-aluminum alloy (Raney alloy) and aqueous alkali bring about a rupture of the carbon-sulfur linkage. In this case, the quantity of hydrogen available may be much more than that in the desulfurization with Raney nickel.

---

[15] P. L. Bethge, *Anal. Chem.*, **28**, 119 (1956).

[16] H. Kitagawa and N. Shibata, *Bunseki Kagaku*, **7**, 284 (1958).

[17] A. D. Horton and P. F. Thomason, *Anal. Chem.*, **28**, 1326 (1956).

[18] C.-E. Liau, K. Yamashita, and M. Matsui, *Agr. Biol. Chem.* (Tokyo), **26**, 624 (1962).

[19] D. Papa, E. Schwenk, and H. F. Ginsberg, *J. Org. Chem.*, **14**, 723 (1949).

These facts and considerations prompted us to use Raney alloy *per se* in aqueous formic acid. Table 1 shows that, under conditions similar to those used with Raney nickel, the treatment with Raney alloy containing 50% Al by weight leads to an almost complete desulfurization, even when the Ni/S ratio is 0.8 : 1. In contrast with the usual desulfurization, which is carried out in a neutral medium, a large portion of the sulfur eliminated from the substrate during the reaction is transformed into hydrogen sulfide and is released from the reaction mixture. Only a small portion of the sulfur remains in the system as nickel sulfide. When the Ni/S ratio was 0.8 : 1, more than 90% of the sulfur in the starting material was recovered as hydrogen sulfide and nickel sulfide. It should be noted that the gram atoms of sulfur removed amount to more than the nickel used. Furthermore, the value of the Ni/S ratio can be greatly diminished by using a Raney alloy which contains more than 50% aluminum. The results are shown in Table 2. The higher the content of aluminum in the alloy, the smaller the Ni/S ratio required for the desulfurization. By using an alloy which is 70% aluminum, the desulfurization yield reached 90%, even when the Ni/S ratio was 0.2 : 1.

Table 2. Desulfurization reactions of I with Raney alloy in 80% formic acid

Ni-Al alloy	Ni/S	Yield of VI		Sulfur in crystal %	Desulfurization yield, %[a]
		Crystal	Mother liquor		
Al 58%	0.50	77	9	0.08	94
	0.40	82	8	0.27	94
	0.30	66	10	0.47	91
	0.20	38	17	4.69	72
Al 70%	0.30	79	6	—	92
	0.25	77	5	—	91
	0.20	82	3	—	90

a) $\dfrac{\text{H}_2\text{S(mol) evolved} + \text{S(atom) in NiS}}{\text{S(atom) in starting material}} \times 100$

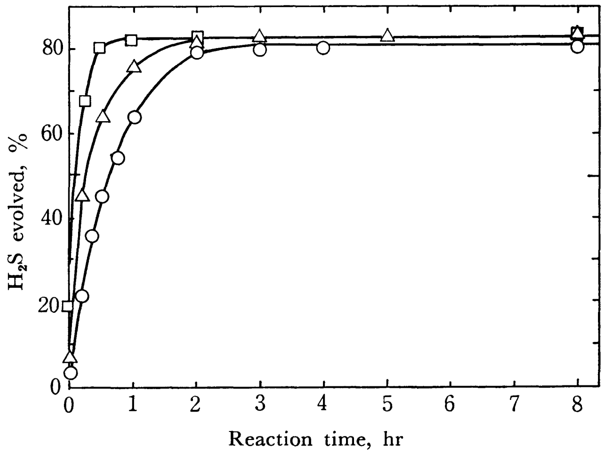


Fig. 1. Effect of Al content on the evolution rate of H_2S ($Ni/S=0.30$, in 80% HCOOH).
○ Al 58%; △ Al 65%; □ Al 70%

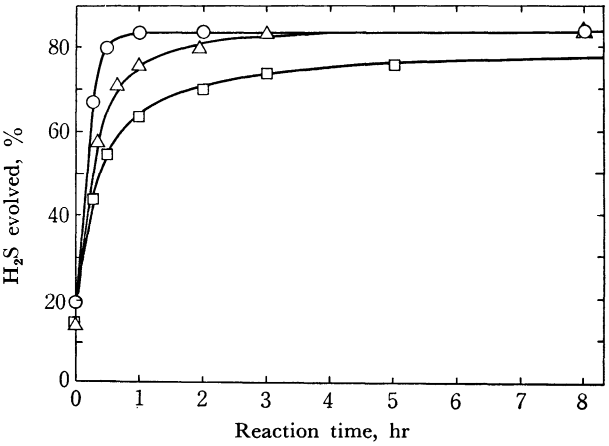


Fig. 2. Effect of the amounts of alloy on the evolution rate of H_2S (Al content of alloy: 70%, in 80% HCOOH).
○ $Ni/S=0.30$; △ $Ni/S=0.25$; □ $Ni/S=0.20$

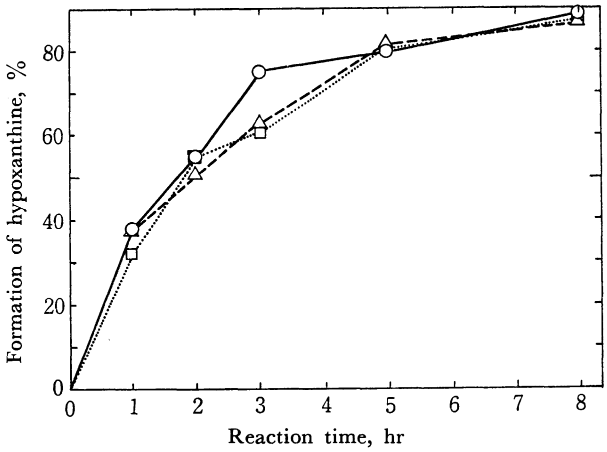


Fig. 3. Effect of the amounts of alloy on the formation rate of hypoxanthine (Al content of alloy: 70%, in 80% HCOOH).
○ $Ni/S=0.30$; △ $Ni/S=0.25$; □ $Ni/S=0.20$

Figure 1 shows the dependence of the hydrogen sulfide evolution rate on the aluminum contents of the alloys used. If the Ni/S ratio is constant, the higher the content of aluminum, the more rapid the rate of the evolution of hydrogen sulfide.[20]

Figure 2 shows the effect of the Ni/S ratio on the evolution rate of hydrogen sulfide in the reactions with the alloy containing 70% aluminum in 80% formic acid. The effect of the Ni/S ratio on the hypoxanthine formation rate is indicated in Fig. 3. It can be seen by a comparison of Fig. 3 with Fig. 2 that the rate of the formation of hypoxanthine is independent of the Ni/S ratio, unlike the rate of the evolution of hydrogen sulfide, and that the former is smaller than the latter. These facts suggest that if the requirements for the desulfurization are satisfied, the desulfurization rate can not be rate-determining. The rate-determining step is assumed to be the cyclization step of V to VI for the following reasons: 1) it is well known that the formylation reactions of I to II[6,7] and of IV to V[14] are very rapid in hot formic acid; 2) the cyclization reaction

---

[20] It should be remembered that the rate of the evolution of hydrogen sulfide may not necessarily represent the rate of the C–S bond cleavage, because the former rate depends on the rate with which hydrogen carries hydrogen sulfide out of the reaction vessel. As expected, the rate of the evolution of hydrogen becomes more rapid as the quantity of aluminum increases.

of II to III is said to be more difficult than that of V to VI[21]; 3) the ultraviolet absorption spectrum of a spot (R_f 0.61, solvent system 5 N acetic acid : 1-butanol=1 : 2) which appeared on the paper-chromatogram of the reaction mixture was identical with that of V, and 4) V was recovered in a 5% yield from the mother liquor of hypoxanthine after 8 hours of reaction.

Figure 4 demonstrates the effect of the addition of aluminum or iron powder on the desulfurization reaction in which Raney alloy (Ni/S ratio=0.2 : 1) was used. These metallic powders clearly revealed an accelerating effect, though they were not so effective as aluminum in the Raney alloy. Thus, it was established that hydrogenolytic desulfurization in aqueous formic acid does not always require a stoichiometric amount or an "excess" of nickel, provided that a sufficient amount of metallic aluminum or iron is present.

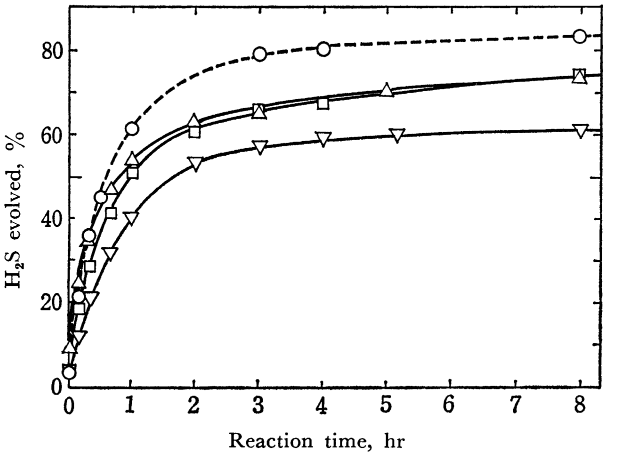


Fig. 4. Effect of addition of Al or Fe powder (Al content of alloy: 58%, in 80% HCOOH).

Ni/S	Additive	Total gram-eqs. of metals
○ 0.30	—	1.04
△ 0.20	Fe	1.04
□ 0.20	Al	1.04
▽ 0.20	—	0.70

As will be described later (see Table 3), metallic aluminum or iron by itself has little desulfurizing activity. Therefore, we propose the following mechanism for the desulfurization reaction with the Raney nickel alloy in acidic media (Eqs. (3) to (9)):

$$\text{-}\underset{|}{\text{Ni}}\text{-}\underset{|}{\text{Al}}\text{-} + H^+ \rightarrow \text{active Ni} + Al^+ + H \quad (3)$$

$$\text{-}\underset{|}{\text{Ni}}\text{-}\underset{|}{\text{Ni}}\text{-} + RSH \rightarrow \text{-}\overset{|}{\underset{|}{\text{Ni}}}\text{-R} + \text{-}\overset{|}{\underset{|}{\text{Ni}}}\text{-SH} \quad (4)$$

$$\text{-}\overset{|}{\underset{|}{\text{Ni}}}\text{-R} + H \rightarrow \text{-}\overset{|}{\underset{|}{\text{Ni}}} + RH \quad (5)$$

$$\text{-}\overset{|}{\underset{|}{\text{Ni}}}\text{-SH} \rightarrow \text{Ni sulfide} + H \quad (6)$$

$$\text{-}\overset{|}{\underset{|}{\text{Ni}}}\text{-SH} + H^+ \rightarrow Ni^+ + H_2S \quad (7)$$

$$Ni^+ + Al \rightarrow Ni + Al^+ \quad (8)$$

$$\begin{array}{l} \text{-}\overset{|}{\text{Ni}}\text{-SH} + H^+ \rightarrow Ni + H_2S + Al^+ \\ \;\;| \\ \text{-}\underset{|}{\text{Al}} \end{array} \quad (9)$$

To simplify, let us consider the transfer of only one electron.

As is shown in Eq. (3), the Raney nickel alloy reacts with the acid to provide an active catalyst and hydrogen.

The substrate is adsorbed on the nickel surface to give an organic radical (Eq. (4)), which subsequently changes into the final product by combining with a hydrogen atom (Eq. (5)). On the other hand, the sulfur atom bonded to the nickel atom, depending upon the acidity of the medium, yields nickel sulfide (Eq. (6)) or gives a nickel ion and hydrogen sulfide (Eq. (7)). The nickel ion produced in the latter process is again reduced into metallic nickel by metals (these will hereafter be called "auxiliary metals") having a larger tendency of ionization, such as aluminum or iron.

Therefore, the auxiliary metals seem to play two roles, that of a hydrogen-atom supplier for the substrate (Eq. (3)) and that of a reducing agent for ionized nickel (Eq. (8)). Such a regenerating mechanism of metallic nickel with catalytic activity can be operative only when two requirements are satisfied—that metals having a larger tendency of ionization than nickel are present and that the reaction medium is acidic enough to liberate hydrogen sulfide from nickel sulfide. In the case of the Raney alloy, electron transfer from aluminum to nickel may occur within the crystal lattice of the alloy as at the local cells in the corrosion of metals (Eq. (9)). In brief, nickel is considered to be protected by the auxiliary metals against inactivation due to ionization.

If the regenerating mechanism of nickel described above is correct, it will not always be necessary to use nickel in the metallic state, that is, it will be possible to use, for the same purpose, many combinations of appropriate nickel *salts* and metals with oxidation-reduction potentials more negative than that of nickel. This expectation was realized, as is shown in Fig. 5

TABLE 3. DESULFURIZATION REACTIONS OF I WITH DESULFURIZING AGENTS OTHER THAN RANEY ALLOY IN 80% FORMIC ACID

A	B[a]	A(atom)/ S(atom)	H_2S evolved, %
$Ni(HCO_2)_2\cdot2H_2O$	Fe powder	0.5	80
$CoCl_2\cdot6H_2O$	Fe powder	0.5	80
$CuSO_4\cdot5H_2O$	Al powder	0.5	7[b]
$Pb(AcO)_2\cdot3H_2O$	Fe powder	0.5	0[b]
$Cd(AcO)_2\cdot2H_2O$	Fe powder	0.5	2[b]
$Ni(HCO_2)_2\cdot2H_2O$	Zn powder	0.5	7[b]
—	Al powder	—	6[b]
—	Fe powder	—	20
—	Zn powder	—	2[b]

a) 1.74 equivalents to the gram-atom of sulfur in the substrate
b) No hypoxanthine was detected in reaction mixture.

---

[21] R. K. Robins, K. J. Dille, C. H. Willits, and B. E. Christensen, *J. Amer. Chem. Soc.*, **75**, 263 (1953).

TABLE 4. FATE OF NICKEL AND ALUMINUM (IN 80% FORMIC ACID)

			Ni-Al alloy (Al 58%)				$Ni(HCO_2)_2$+Al
Ni/S			0.50	0.40	0.30	0.20	0.50
Ni	Before the reaction		9.29g	7.41g	5.56g	3.71g	9.29g
	After the reaction	a	2.55	2.35	1.62	2.05	1.78
		b	1.74	1.38	1.29	0.51	0.90
		c	3.54	2.74	2.29	0.00	6.02
		d	0.17	0.14	0.33	1.01	0.03
		total	8.00	6.61	5.53	3.57	8.73
Al	Before the reaction		12.81	10.23	7.69	5.13	21.35
	After the reaction	a	7.69	6.49	5.82	4.05	14.33
		c	3.89	1.77	1.09	0.35	5.54
		d	0.07	0.08	0.12	0.21	0.05
		total	11.65	8.34	7.03	4.61	19.92

a) In soluble in the reaction mixture and water-soluble
b) In NiS
c) Metallic
d) Soluble in the reaction mixture

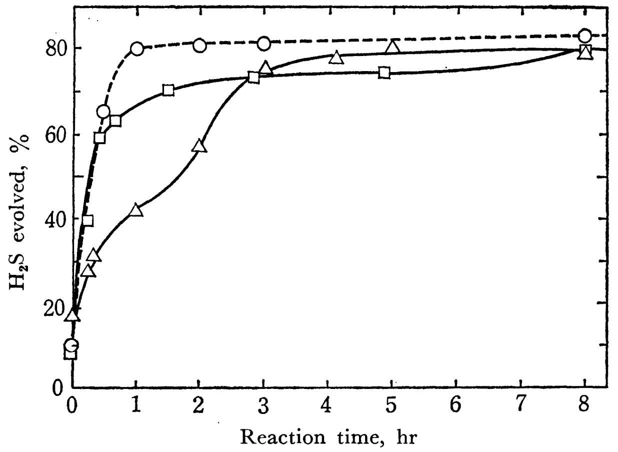


Fig. 5. Desulfurization with Ni or Co salt and Fe powder (in 80% HCOOH).
○ Ni-Al alloy (Ni/S=0.50);
△ $Ni(HCOO)_2 \cdot 2H_2O$ (Ni/S=0.50)+Fe;
□ $CoCl_2 \cdot 6H_2O$ (Co/S=0.50)+Fe

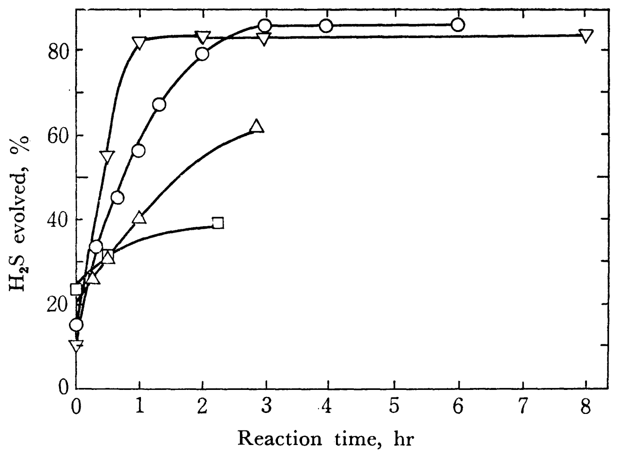


Fig. 6. Desulfurization in various acids.
(Al content of alloy: 58%, Ni/S=0.50)
▽ 80% HCOOH; ○ 1N H_2SO_4; △ 1N HCl; □ 2N HCl

and Table 3. The combination of nickel formate and iron powder caused about 80% of the theoretical yield of hydrogen sulfide to evolve. A similar result was also obtained when the combination of nickel formate and aluminum powder was used. Furthermore, even when a cobaltous chloride-iron powder system was used, a smooth desulfurization reaction was observed.[22]

Table 4 shows the fate of nickel and aluminum after the desulfurization reactions. It is clearly shown in the last column that a considerable portion of the nickel ions in the nickel formate was reduced to metallic nickel. When the desulfurization reaction was incomplete, as when the Ni/S ratio was 0.2 : 1 (see Table 2), little or no metallic nickel and aluminum remained after the reaction.

All of the desulfurization reactions described above were carried out in aqueous formic acid. Hence, there is a possibility that the formic acid might play a specific role in the reductive desulfurization. This is not the case, however. The desulfurization reaction was also successfully performed in some mineral acids, as is shown in Fig. 6. (In these cases, the product was not, of course, hypoxanthine, but 4,5-diamino-6-hydroxypyrimidine.) In particular, 1 N sulfuric acid was a good medium. Hydrochloric acid was inferior to sulfuric acid as a reaction medium. This disadvantage seems to be accounted for by the fact that hydrochloric acid allows a large portion of hydrogen to evolve before the reaction temperature required for desulfurization is reached. Therefore, the kinds and concentrations of acids must be selected so that the reaction of the auxiliary metals with acids does not proceed too violently below the temperature required for the desulfurization.

For the same reason, it is necessary to select the auxiliary metals, which should have a more negative oxidation-reduction potential than nickel (or cobalt), from such metals that the rate of the evolution of hy-

---

[22] Since the presence of the auxiliary metals in the course of the desulfurization reaction is essential for the present purpose, the direct addition of the nickel or cobalt salt and the auxiliary metal to the reaction mixture is of greater advantage than the use of an Urushibara catalyst[23] prepared in the usual way.

[23] Y. Urushibara, S. Nishimura, and H. Uehara, This Bulletin, **29**, 446 (1956).

drogen at a given acidity is not so fast as the rate of desulfurization. Zinc powder was, for example, unsuitable as an auxiliary metal, because it reacts with 80% formic acid so rapidly that the evolution of the theoretical amount of hydrogen was completed in the course of raising the temperature (below 60°C) (see Table 3).

Table 3 also reveals that the metallic salts other than nickel and cobalt salts, that is, cupric sulfate, lead diacetate, and cadmium diacetate, have little or no desulfurizing activity. Aluminum or zinc powder by itself shows little activity. As for iron powder, the desulfurization reaction was observed, but to a lesser extent.

Of great interest is the fact that the metals effective for the desulfurization in the present conditions are confined to the Group VIII metals in the periodic table. The question of why the Group VIII metals can dissociate the carbon-sulfur bond in the adsorbed compound into radicals is an important problem to be solved in the future.

In conclusion, the present procedure can be expected to provide a convenient technique for the desulfurization of acid-stable compounds not only in industry, but also in the laboratory.