

In terms of the fraction of metal atoms exposed to the reactants, Aben and coworkers found an approximate two-fold increase in activity for benzene hydrogenation on nickel/silica when this fraction was raised from 0.1 to 0.2. However, a direct comparison with these results is obscured since the earlier workers used a much greater hydrogen pressure, individual catalysts with a wide spectrum of crystallite sizes ranging from 10 to 200 Å and an impregnation procedure for catalyst preparation which would be expected to yield a catalyst series with a lower range of nickel content than those used in the present work.

The hydrogenation of the diolefin 1,3-butadiene produced as its main products the monoolefins 1-butene, *trans*-2-butene, and *cis*-2-butene with no evidence of the occurrence of complete hydrogenation to *n*-butane. These findings are in agreement with earlier work (Phillipson et al., 1969; Oliver et al., 1973) when results were not specifically related to metal crystallite size.

There is a general trend for the selectivity toward 1-butene formation to increase with both increase in temperature and nickel content. Previously, a similar effect of temperature was detected and explained by a decrease in the availability of adsorbed hydrogen which would tend to favour the formation of 1-butene (Bond et al., 1965). The amount of this isomer produced would also be expected to increase with nickel content if both Ni(II) and Ni(III) oxidation states occur in the nickel precipitate prior to reduction since it has been concluded from mechanistic studies that this type of surface is most likely to coordinate the intermediate 1-methyl- π -allyl ligand to a metal atom (Oliver et al., 1973).

Conclusions

In the hydrogenation of benzene, toluene, and 1,3-butadiene, nickel-on-silica catalysts, prepared without thermal sintering, exhibit a pronounced trend for reactions rates based on catalyst mass to increase progressively with (i) an

increase in catalyst nickel content, (ii) an increase in the average nickel crystallite size, and (iii) a decrease in nickel metal area.

The selectivity of the catalyst series toward 1-butene formation increases with increase in the reaction temperature from 85 to 175°C and with an increase in the catalyst nickel content from 4.32 to 79.43%.

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Literature Cited

- Aben, P. C., Platteeuw, J. C., Stouthamer, B., *Proc. Int. Congr. Catal.*, **4th**, (1970).
 Bond, G. C., Webb, G., Wells, P. B., Winterbottom, J. M., *J. Chem. Soc.*, **3218** (1965).
 Borisova, M. S., Dzis'ko, V. A., Bulgakova, Yu. O., *Kinet. Catal.*, **12**, 344 (1971).
 Boudart, M., *Adv. Catal.*, **20**, 153 (1969).
 Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., Harkins, C. G., *J. Catal.*, **6**, 92 (1966).
 Carter, J. L., Cusumano, J. A., Sinfelt, H. H., *J. Phys. Chem.*, **70**, 2257 (1966).
 Coenen, J. W. E., van Meerten, R. Z. C., Rijntjen, H. T., *Proc. Int. Congr. Catal.*, **5th**, (1973).
 Dzis'ko, V. A., Noskova, S. P., Karachiev, L. G., Borisova, M. S., Bolgova, V. G., Tyulikova, T. Ya., *Kinet. Catal.*, **13**, 366 (1972).
 Hill, F. N., Selwood, P. W., *J. Amer. Chem. Soc.*, **71**, 2522 (1949).
 Madden, W. F., Kemball, C., *J. Chem. Soc.*, 302 (1961).
 McCaffrey, E., Ph.D. Thesis, The Queen's University of Belfast, N. Ireland, 1972.
 Oliver, R. G., Wells, P. B., Grant, J., *Proc. Int. Congr. Catal.*, **5th**, (1973).
 Phillipson, J. J., Wells, P. B., Wilson, G. R., *J. Chem. Soc.*, 1351 (1969).
 Ross, R. A., McBride, G. B., *Chem. Ind.*, 1504 (1960).
 Ross, R. A., Walsh, B. G., *J. Appl. Chem.*, **11**, 469 (1961).
 Scholten, J. J. F., van Montfort, A., *J. Catal.*, **1**, 85 (1962).
 Taylor, W. F., Staffin, H. K., *Trans. Faraday Soc.*, **63**, 2309 (1967).
 van Hardeveld, R., Hartog, F., *Adv. Catal.*, **22**, 75 (1972).
 Yates, D. J. C., Taylor, W. F., Sinfelt, J. H., *J. Amer. Chem. Soc.*, **86**, 2996 (1964).

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Lanthanum Titanate Catalyst—Sulfur Dioxide Reduction

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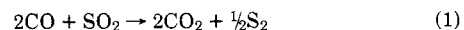
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Preliminary studies on dry gases indicate that lanthanum titanate is an active catalyst for the reduction of sulfur dioxide to elemental sulfur by means of carbon monoxide. This material is characterized by a low rate of carbonyl sulfide (COS) formation by further reduction of the sulfur initially produced. Catalysts previously studied do not possess this ability. Minimizing COS formation is important in stack gas purification systems because this substance is extremely toxic.

Introduction

No substantial commercial experience exists for catalysts employing CO for the reduction of SO₂. Laboratory studies have been published by Khalafalla et al. (1971, 1972) using an iron oxide catalyst supported on alumina and by Ryason and Harkins (1967), Quirido and Short (1973), Quinlan et al. (1973a) and Kasaoka et al. (1973), all using a copper

supported catalyst. Further studies by Quinlan et al. (1973b) and Goetz et al. (1974) included screening of a number of catalysts for simultaneous reduction of SO₂ and NO with CO. In all the studies that so far have been reported it was found that in addition to the desired reaction



a second reaction occurs between carbon monoxide and ele-

Table I. Stability of Metallic Oxides (in Increasing Order of Stability in Presence of Sulfur)

Element	Formula ^a	Heat of formation difference, kcal/(mol of O ₂ or S ₂ per mol of oxide), (-ΔH ₂₉₈ ^o oxide) - (-ΔH ₂₉₈ ^o sulfide)
Copper	MC	50.0
Cadmium	MC	51.4
Lead	MC	59.8
Barium	MC	66.0
Zinc	MC	70.0
Nickel	MC	70.6
Cobalt	M ₃ C ₄	70.7
Strontium	MC	72.2
Manganese	MC ₂	74.8
Molybdenum	MC ₂	79.6
Iron	MC	80.8
Calcium	MC	83.2
Cerium	M ₂ C ₃	89.6
Tungsten	MC ₂	92.5
Lanthanum	M ₂ C ₃	99.0
Magnesium	MC	121.4
Titanium	MC ₂	145.5
Aluminum	M ₂ C ₃	151.4
Beryllium	MC	174.4

^a M = cation; C = anion, oxygen, or sulfur.

mental sulfur that is produced during the course of the reaction



The production of carbonyl sulfide (COS) usually proceeds to a substantial extent on the catalysts previously studied. This substance is highly toxic and thus is undesirable as an effluent contaminant.

According to a patent by Parish et al. (1968), cobalt and molybdenum sulfides catalyze the formation of COS from CO and sulfur. Therefore, a preliminary study was made of the thermodynamics of oxide conversion to sulfide in order to evaluate possible catalyst candidates for SO₂ reduction. Small traces of oxygen may be present in the gases being fed to a catalytic reactor so it is difficult to accurately estimate the partial pressure of oxygen in the thermodynamic study. It was therefore decided to simply investigate the relative stability of various oxides with respect to the formation of the corresponding sulfides. Actually the sulfide formation will depend upon the relative partial pressures of oxygen and sulfur in the gases that are in contact with the catalyst, but the tendency to form sulfides may be related to possible COS formation.

A useful reference in making these calculations is Kubachewski et al. (1967). Detailed calculation of the equilibrium constants showed that in the reaction considered, the entropy contribution to the free energy change is relatively small. Thus, the tendency for sulfide formation is measured generally by the difference between the heat of formation of the oxide and the corresponding sulfide for a given metal. If these differences are expressed in terms of a unit mole of oxygen or sulfur, it is possible to list the elements in increasing order of their stability toward sulfide formation and thus their possible usefulness in catalyst formation. Table I presents such a compilation for a number

Table II. Tolerance Factor for LaTiO₃

Element	Radius, Å
La	1.35
Ti	0.61
O ²⁻	1.35
$t = (1.35 + 1.35)/[\sqrt{2}(0.61 + 1.35)] = 0.97$	

of representative oxides and corresponding sulfides for which data are available.

Some binary oxides high in stability were screened as SO₂ reduction catalysts but did not exhibit exceptional activity. Therefore it was decided to try ternary and quaternary oxides. Early studies of Parravano (1952) indicated the possibility of perovskites in the oxidation of carbon monoxide. Later Libby (1971) pointed out the potential of lanthanum cobalt oxide as a catalyst for controlling automotive exhaust pollution, following Meadowcraft's report (1970) that strontium doped lanthanum cobalt oxide (La_{0.8}Sr_{0.2}CoO₃) equaled platinum as an oxygen electrode. Bauerle et al. (1972) have reported results of tests on these mixed oxides which confirm their activity for CO oxidation in air and reduction of NO by CO.

Perovskite structure oxides represent a wide class of inorganic compounds of the general formula ABO₃ where A and B are appropriate cations. Treatises such as that of Wells (1962) give formulas which define the range of atomic radii which must be involved if the perovskite structure is to be obtained. The structure is defined in terms of a tolerance factor

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad (3)$$

where r_A , r_B , and r_O are the atomic radii of the elements A, B, and oxygen. The ideal cubic lattice corresponds to $t = 1$. Actually the perovskite structure is stable in the range $0.75 < t < 1.0$. In addition to satisfying this constraint, the A and B cations must themselves be stable in twelvefold (12, or 8 + 4, or 6 + 6) and sixfold coordination. This sets the lower bounds for the cation radii which in oxides are $r_A > 0.90$ Å and $r_B > 0.51$ Å.

Of the elements listed in Table I only lead, barium, strontium, cerium, and lanthanum have atomic radii greater than 0.9 Å. Lanthanum and cerium seem to be much superior to the other cations with regard to stability toward sulfide formation. Because of price considerations lanthanum appears to be a better candidate than cerium although probably any of the rare earth elements could be employed as the A cation.

With the choice of the A cation fixed, the B cation must have a valence of +3 in one of its valence states. The possible perovskites based on lanthanum being the A cation are: LaAlO₃, LaCoO₃, LaFeO₃, LaNiO₃, and LaTiO₃. Again referring to Table I, titanium is obviously the element of choice. Lanthanum titanate (LaTiO₃) also comes close to meeting the requirements for the ideal cubic perovskite structure as shown in Table II.

Catalyst Formulation and Characterization

The catalyst was prepared by the coprecipitation method employing La(NO₃)₃ and TiCl₄. The addition of a small proportion of calcium was found to improve stability and the kinetic tests reported here correspond to the approximate formulation Ca_{0.01}La_{0.9}TiO₃. The washed precipitate was mixed with an appropriate proportion of CaCO₃, dried, and calcined at 900°C under a hydrogen atmosphere. Perti-

Table III. X-Rated Diffraction Patterns Related to Catalyst

TiO ₂ (rutile)		TiO ₂ (anatase)		La ₂ O ₃		La ₂ O ₃ ·TiO ₂		La ₂ O ₃ ·2TiO ₂ (pyrochlore)		2La ₂ O ₃ ·9TiO ₂		LaTiO ₃ (perovskite)		Catalyst Ca _{0.01} La _{0.9} TiO ₃	
dÅ	I, %	dÅ	I, %	dÅ	I, %	dÅ	I, %	dÅ	I, %	dÅ	I, %	dÅ	I, %	dÅ	I, %
								4.19	44					4.22	35
						3.59	30	3.83	10	3.36	100	3.92	W*		
		3.51	100	3.41	60			3.39	10	3.28	82				
3.24	100					3.21	100	3.21	63	3.19	20			3.21	63
								3.16	26					3.18	45
				3.06	50	3.13	75	3.11	13					3.13	35
				2.97	100	3.09	32	2.99	100	3.05	20			3.00	100
								2.78	49	3.00	28	2.78	S*	2.78	88
2.49	70					2.74	38	2.71	38					2.71	68
2.31	20	2.43	10											2.64	40
2.26	30	2.37	50	2.27	50					2.54	41	2.27	M*	2.25	35
2.19	40	2.33	10											2.10	35
2.05	30													2.06	30
2.01	20			1.96	60							1.97	S	1.95	68
1.88	40	1.89	90	1.75	50							1.76	W	1.89	30
1.78	20	1.70	70	1.70	10							1.60	S	1.60	37
1.68	100	1.66	70	1.65	40							1.39	M		
		1.45	70									1.31	W-		
		1.36	60									1.24	M		
		1.34	60												
		1.26	70												
		1.25	20												
		1.16	60												

nent physical properties are bulk density, 1.5 g/cm³ and surface area, 16 m²/g.

Active catalysts were characterized by X-ray diffraction. A good reference on X-ray crystallography is a text by Cullity (1956).

In reacting mixtures of TiO₂ and La₂O₃ a range of compounds is possible. Thus in an unreduced system La₂O₃·TiO₂, La₂O₃·2TiO₂, and 2La₂O₃·9TiO₂ have been identified by MacChesney and Sauer (1962). When a mixture containing a slightly lower ratio of La:Ti than unity is allowed to react, the product should contain La₂O₃·2TiO₂ and 2La₂O₃·9TiO₂ at complete reaction. If this mixture is reduced completely the La₂O₃·2TiO₂ should be converted to the perovskite LaTiO₃ (Kestigian and Ward, 1954).

Table III presents appropriate X-ray diffraction data for all these compounds and the catalyst. The La₂O₃ and TiO₂ are identified as expected noting that the TiO₂ corresponds to the anatase rather than the rutile crystal form of titanium oxide. The catalyst sample shows a very prominent line at 3.00 dÅ, 100% and a strong line at 3.21 dÅ, 63%. These correspond to La₂O₃·2TiO₂ with a strong line of 2.98 dÅ, 100%, a weaker line of 3.21 dÅ at 63%. This seems to establish the presence of La₂O₃·2TiO₂, as expected if reaction by calcination is significant. The second most prominent line in the catalyst sample is 2.78 dÅ, 88%. There is a prominent line at 1.95 dÅ, 68%. These lines correspond to perovskite of LaTiO₃ composition with 2.78 dÅ, 100% and 1.97 dÅ at 100%. Thus there is evidence of considerable perovskite in the active catalyst.

Prominent lines corresponding to the La₂O₃ and rutile structures are not present in the catalyst sample indicating that calcination is conducted at a sufficiently high temperature to secure complete reaction.

Lanthanum titanate may exist in a perovskite structure at lower La:Ti ratios than one. These structures correspond to perovskites with oxygen defect structure. Lanthanum ti-

tanates with perovskite structures have been identified over the range La_(2/3+x)TiO₃, where x may have values from 0 to $\frac{1}{3}$. With $x = 0$, the titanium cation is in the +4 valence state, corresponding to a lattice with one-third of the lanthanum positions vacant. With $x = \frac{1}{3}$, the titanium would be in the +3 valence state. Among the catalyst formulations tested those with a ratio of La:Ti close to unity have the highest activity. Thus, the catalyst activity seems to correspond to titanium in the +3 valence.

Experimental Procedure

A conventional flow reactor was employed for catalyst evaluation. It was operated integrally, isothermally, and essentially at atmospheric pressure. The reactor was fabricated from Vycor and was externally heated by an electric resistance furnace.

The feed and product gas streams were analyzed in a Perkin-Elmer Model 900 gas chromatograph equipped with dual $\frac{1}{8}$ in., 12 ft long stainless steel columns packed with 60/80 mesh Chromasorb 102 provided by Perkin-Elmer. The temperature program for the analysis consisted of maintaining a temperature of -70°C for 4 min, followed by a linear increase at a rate of 24°C/min until a final temperature of 110°C was obtained. This temperature was maintained until the SO₂ was eluted. The entire analysis was performed in approximately 20 min. It was possible to analyze for N₂, CO, CO₂, H₂S, COS, and SO₂ using this technique.

Details of the experimental procedures employed and of the screening program are given by Kundrath (1973). Generally between 1.5 and 5 g of catalyst was employed in the evaluation experiments.

As a basis for comparison and in order to gain insight into the phenomena occurring during reaction several conventional catalysts, similar to those evaluated by previous investigators, were tested. These included a copper catalyst

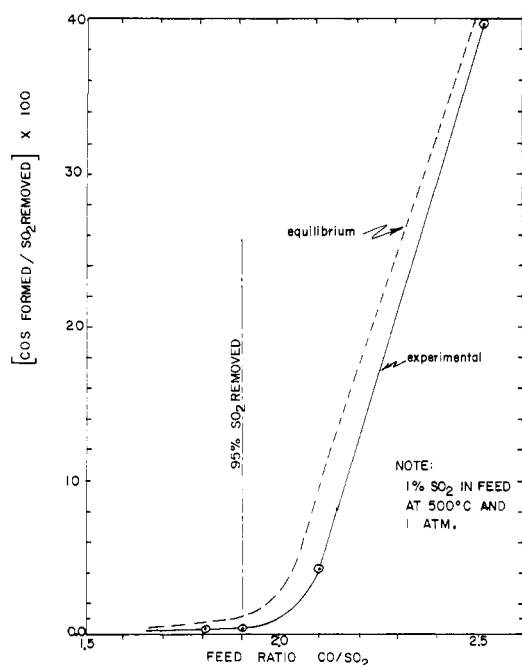


Figure 1. Effect of ratio CO/SO₂ on COS production.

(supplied by Harshaw, Cu-0203) containing 78% CuO and 20% Cr₂O₃ and an iron catalyst (supplied by Harshaw, Fe-0301) containing 20% Fe₂O₃ on an activated alumina support. In the studies in which these catalysts were evaluated it became apparent that sulfide formation was taking place during the reaction. Acidification of the spent catalyst resulted in the liberation of H₂S. The lanthanum titanate catalyst did not give any evidence of such sulfide formation.

Results

In view of the importance of minimizing the production of COS, a special series of experiments was conducted in which the ratio of CO to SO₂ was varied in mixtures of these gases with nitrogen as a diluent. The complete conversion of SO₂ requires two moles of CO. The results of this study are presented in Figure 1.

As previous investigators have found, the tendency toward formation of COS increases with increase in the CO to SO₂ ratio in the reacting stream. In the case of the lanthanum titanate catalyst the production of COS does not become significant until the CO to SO₂ ratio nears 2.0. Figure 1 shows the effect of increasing CO/SO₂ ratios when reacting mixtures containing 1% SO₂ by volume. Also shown is the total sulfur removal corresponding to equilibrium, using the JANAF Tables (1971) as a source of thermodynamic data. With a feed corresponding to CO/SO₂ ratios of approximately 1.9, it is possible to obtain 95% removal of sulfur dioxide from this gas.

Additional studies were conducted at 500°C to establish the kinetics of the operation at varying partial pressures of carbon monoxide and sulfur dioxide. Table IV gives a summary of the data obtained. Results of these studies were correlated by the rate expression, $r = kp_{\text{SO}_2}$, where r is the rate of SO₂ reacted in (mol of SO₂ removed)/(g of catalyst) (sec) and p_{SO_2} is expressed in mm of Hg. $k = 0.62 \times 10^{-6} \pm 0.09 \times 10^{-6}$. Partial pressure of carbon monoxide appears to have little effect on the rate of reaction, even at very low concentrations of CO relative to SO₂.

Discussion

Our results for the rate of SO₂ conversion and its first-

Table IV. Summary of Conversion Data at 500°C

CO/SO ₂ feed ratio	% SO ₂ inlet	(V/V' - hr) × 10 ⁻⁴	% SO ₂ red.	(mol of COS formed/ mol SO ₂ removed) × 100
2.1	0.3	12.60	18.30	nd ^a
2.1	0.3	4.45	55.60	nd
2.1	0.3	.70	100.00	nd
2.1	1.0	5.66	67.50	nd
2.1	1.0	12.50	19.60	nd
2.1	1.0	10.30	24.40	nd
2.1	1.0	8.12	58.00	nd
2.1	1.0	4.90	55.00	nd
2.1	1.0	1.90	72.50	5.3
1.8	1.0	8.95	8.30	5.0
1.8	1.0	12.30	6.49	nd
1.8	1.0	6.50	22.70	nd
1.8	1.0	3.90	36.20	nd
1.8	1.0	2.70	62.40	nd
2.1	5.0	9.50	38.00	9.1
2.1	5.0	12.40	29.30	15.7
2.1	5.0	8.50	41.30	13.5
2.1	5.0	5.40	55.60	13.3
2.1	5.0	1.90	70.00	10.2
1.9	5.0	5.00	61.80	0.3
1.9	5.0	12.75	37.50	0.3
1.9	5.0	9.90	47.00	0.3
1.9	5.0	7.30	52.30	0.3
1.9	5.0	3.66	78.00	0.3
1.9	1.0	12.60	27.80	0.3
1.9	1.0	9.50	37.80	0.3
1.9	1.0	7.66	43.60	0.3
1.9	1.0	6.70	52.50	0.3
1.9	1.0	2.30	78.60	0.3
1.9	1.0	5.30	58.20	0.3
1.9	0.3	2.30	87.40	nd
1.9	0.3	9.00	33.00	nd
1.9	0.3	0.75	96.00	0.3
1.9	0.3	4.30	50.80	nd
1.9	0.3	8.30	41.00	nd
1.9	0.3	6.80	39.50	nd
1.9	0.3	4.50	54.50	nd
1.9	0.3	3.80	68.50	nd
1.9	0.3	4.90	51.80	nd
2.5	1.0	2.15	97.10	37.2
2.5	1.0	8.30	57.50	20.2

^a Not determined.

order dependence on SO₂ concentration are comparable with the comprehensive kinetic study reported by Quinlan et al. (1973a) for a copper-alumina catalyst. These authors also indicated that the production of COS is a function of SO₂ conversion, without significant dependence on the ratio of CO/SO₂ in the reacting gases. This is not the case for our catalyst and in fact the limited data we have obtained indicate first-order dependence of COS formation on CO partial pressure.

The dual bed system proposed by Sood and Kittrell (1974) in which undesirable COS formed in the first bed reacts with SO₂ in a second bed to yield sulfur represents an alternative procedure which may not be necessary when using a catalyst of the type reported here. In order to establish the practicality of this system further studies will be required using gases containing the other flue gas components, O₂, CO₂, and H₂O. Such studies are in progress at our laboratory.

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Literature Cited

Bauerle, G. L., Thomas, N. T., Nobe, K., *Chem. Eng. J.*, **4**, 199 (1972).
Cullity, B. D., "X-Ray Diffraction", Addison-Wesley, Reading, Mass., 1956.
Goetz, V. N., Sood, A., Kittrell, J. R., *Ind. Eng. Chem., Prod. Res. Dev.*, **13**, 110 (1974).
"JANAF Thermochemical Tables", 2nd ed, Bureau of Standards, 1971.
Kasaoka, S., Tsumaki, H., Kochihira, T., *Int. Chem. Eng.*, **13**, 762 (1973).
Kestigian, M., Ward, R., *J. Am. Chem. Soc.*, **76**, 6027 (1954).
Khalafalla, S. E., Foerster, E. F., Haas, L. A., *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 133 (1971).
Khalafalla, S. E., Haas, L. A., *J. Catal.*, **24**, 121 (1972).
Kubachewski, O., Evans, E. L., Alcock, C. B., "Metallurgical Thermochemistry", Pergamon, New York, N.Y., 1967.

Kundrath, M. R., Ph.D. Thesis, New York University, 1974.
Libby, W. F., *Science*, **171**, 499 (1971).
MacChesney, J. G., Sauer, H. A., *J. Am. Ceram. Soc.*, **45**, 416 (1962).
Meadowcroft, D. B., *Nature (London)*, **226**, 847 (1970).
Parish, C. E., Urmey, K. W., U.S. Patent No. 3,416,893 (1968).
Parravano, G., *J. Chem. Phys.*, **20**, 342 (1952).
Quinlan, C. W., Okay, V. C., Kittrell, J. R., *Ind. Eng. Chem., Process Des. Dev.*, **12**, 107 (1973a).
Quinlan, C. W., Okay, V. C., Kittrell, J. R., *Ind. Eng. Chem., Process Des. Dev.*, **12**, 359 (1973b).
Quirido, R., Short, W. L., *Ind. Eng. Chem., Process Des. Dev.*, **12**, 10 (1973).
Ryason, P. T., Harkins, J., *J. Air Pollut. Contr. Ass.*, **17**, 796 (1967).
Sood, A., Kittrell, J. R., *Ind. Eng. Chem., Prod. Res. Dev.*, **13**, 181 (1974).
Wells, A. F., "Structural Inorganic Chemistry", 3rd ed, Oxford University Press, 1962.

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Phenylacetonitriles and Phenylmalononitriles from Toluenes and Cyanogen Chloride

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Phenylacetonitrile and phenylmalononitrile were prepared from toluene and cyanogen chloride in an unpacked flow reactor at temperatures of 590–680°C. Molar ratios of toluene/cyanogen chloride in the range of 4 to 0.7 gave phenylacetonitrile in 80–50% yields and phenylmalononitrile in 0–33% yields, respectively. Other reactor feeds studied included phenylacetonitrile-toluene, phenylacetonitrile, *p*-cyano-, *p*-methoxy, *p*-fluoro-, and *p*-chlorotoluene.

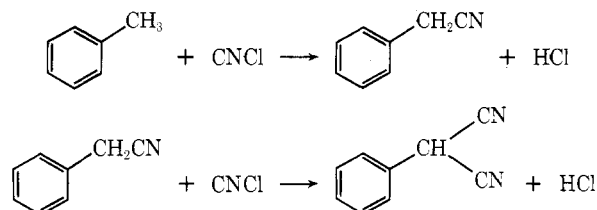
Introduction

Phenylacetonitrile (PAN) is useful as a chemical intermediate. By itself it is useful in the synthesis of pharmaceuticals; salts of its hydrolysis products (phenylacetic acid salts) are used in the manufacture of penicillin and some of the derived esters are used in perfumery. Phenylacetonitrile derivatives in which the ring is substituted with various functional groups such as trifluoromethyl and cyano are reported to be effective herbicides. Phenylacetonitriles are generally made by the reaction of the corresponding benzyl chlorides with sodium cyanide.

While PAN is a commercial product, phenylmalononitrile (PMN) is not. However, PMN can be used as the intermediate in the synthesis of phenobarbital either directly or through conversion to a cyanophenylacetate or phenylmalonate derivative. Currently, the intermediate to phenobarbital is made by carbalkoxylation of phenylacetonitrile.

One of the goals of this work was to study the hot-tube reaction of toluene with cyanogen chloride as a route to these two compounds (PAN and PMN). This reaction was first described by Dixon (1951, 1952) in patents but very

little detail, especially on the preparation of PMN was disclosed. Since both products are produced in one reaction from toluene and cyanogen chloride, studies on reaction temperature, molar ratio, and various methods of product isolation were made. Optimization of PMN yield by using PAN as feed were also examined. A few reactions with *p*-cyano-, *p*-fluoro-, and *p*-chlorotoluene were also run to determine the scope of the reaction.



Experimental Section

Most of the experiments were run in a vertically-mounted 5 cm i.d. × 90 cm long Vycor tube that was encased in an