Reduction of Some Sulfides and Ethers with Aromatic Rings by Electrochemically Generated Solvated Electrons

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The reduction of some sulfides and ethers has been investigated in 0.5 M LiCl–HMPA solutions with and without alcohol (methanol, ethanol, and 2-propanol). Diphenyl sulfide underwent cleavage to produce benzene as the main product. The hydrogenated products of benzene have been obtained in 35 and 50 mol % alcohol solutions, and the increased dependence on ethanol (*i.e.*, H^+) concentrations in the solutions has been established. The cleavage reaction was affected by the ease of α-hydrogen abstraction from the alcohol. The cleavage reaction has been elucidated as proceeding *via* a one-electron transfer mechanism, while the hydrogenation proceeded *via* a two-electron transfer mechanism. The estimation of current efficiencies supports this mechanism. Hexyl phenyl sulfide cleaved in the manner similar to that for diphenyl sulfide with a current efficiency of about 80% whereas only the hydrogenated products were obtained from benzo[*b*]thiophene and dibenzothiophene. Fission of the C–S bond of tetrahydrothiophene has been achieved by this method. Some ethers examined exhibited *approx.* the same behavior as the corresponding sulfides.

Aromatic clusters have been effectively reduced in hexamethylphosphoric triamide (HMPA)–ethanol solutions by electrochemically generated solvated electrons;[1–4] cyclohexane,[2] dihydronaphthalene,[3] and cyclooctane[4] were obtained mainly from benzene, naphthalene, and cyclooctadiene, respectively. The solvent system with HMPA and proton donor appears to provide the most strongly reducing conditions which cannot be achieved by ammonia and amine solvents.[5] Itoh *et al.* have reported the cleavage reactions of aryl decyl ethers in alkali metal–HMPA–THF systems.[6] From these reports, it appears that the solubilization of pitch and coal is efficiently conducted in HMPA solutions by solvated electrons in a manner similar to Benkeser reductions[7] and reductive alkylations.[8]

Prior to the investigation of the reactions of pitch and coal, it is necessary to obtain fundamental information about the reactions using model substances, *i.e.*, the factors which influence the two competitive reactions (the hydrogenation of aromatic clusters and the cleavage of C–X bonds where X denotes oxygen and sulfur atoms) and the reaction mechanisms. To this end, the reduction of some sulfides and ethers which contain aromatic rings has been performed using electrochemically generated solvated electrons in 0.5 M lithium chloride–HMPA solutions with and without alcohol. The reduction of diphenyl sulfide has been investigated thoroughly, since diphenyl sulfide is considered to be the simplest compound containing both aromatic rings and C–X (X: O, S) bonds.

In the investigation, the solvated electrons have been generated electrochemically, since this method achieves the desired rate and amount of solvated electrons easily by controlling the electrolytic current and the quantity of electricity passed, respectively. This feature is a great advantage for mechanistic investigations.

Experimental

Reagents. HMPA was dried on calcium oxide under vacuum and subsequently distilled from calcium hydride at 267 Pa. The middle fraction collected was then stored over molecular sieves 3A in a desiccator containing diphosphorus pentoxide. Methanol, ethanol, and 2-propanol were distilled from magnesium powder activated with iodine, and stored in the same manner as HMPA. The second distillation of the solvents was conducted prior to use. Lithium chloride was dried at 200 °C for 6 h prior to use.

Reactants such as diphenyl sulfide, benzo[*b*]thiophene, dibenzothiophene, tetrahydrothiophene, diphenyl ether, dibenzofuran, and tetrahydrofuran were obtained commercially. Isobenzofuran[9] and hexyl phenyl sulfide[10] were synthesized according to the general procedures. Dibenzothiophene and dibenzofuran were purified by recrystallization from methanol, and the others by distillation. The purity was checked by GLC.

Apparatus. The electrolytic vessel was a special H-type cell of 30 cm^3 total capacity. On the side wall, there were gas outlets with taps and a connecting glass tube to maintain the pressure of gas between the two rooms.

Pt electrodes (1×1 and 3×3 cm) served as cathode and anode, respectively. Before use, they were dipped in saturated sodium hydroxide solution, aqua resia, washed with deionized water, and dried in a desiccator under vacuum.

To generate the solvated electrons, a constant current of 5 mA/cm^2 was supplied by a galvanostat (Hokuto Denko Co., HA-104). When high currents (25 and 50 mA/cm^2) were needed, a DC power supply (Yamabishi Electric Co., Ltd, YVR-550) was used in place of the galvanostat. A linear scanning unit (Hokuto Denko Co., LS-2D) and a HA-104 potentiostat were employed for cyclic voltammometry experiments. The voltammograms were recorded by an X-Y recorder (Yokogawa Electric Works Ltd., 3077). In this case, the potential was measured against Ag/0.1 M $AgClO_4$ in HMPA with a sweep rate of 3.3 mV/s.

Procedure. The preparation of the solution and the electrolysis were performed in a drybox containing diphosphorus pentoxide. The reactant (6 mmol) and HMPA or HMPA–alcohol solution (6 cm^3) containing 0.5 M lithium chloride was poured into each compartment of the cell and immediately the rubber stoppers with the electrodes and gas inlets were set. The cell was placed in a paraffin liquid bath containing Dry Ice and the temperature of the electrolyte maintained at 15 °C. Before electrolysis, dried nitrogen gas was bubbled through the cell for about 30 min, and then the cell was sealed and the catholyte agitated with a magnetic stirrer. The electrolysis was performed with a constant current of 10 mA for 18 h, except when specified otherwise. The amount of electricity passed was checked by a copper coulomb meter. During electrolysis, the cathode potential was not measured, since it was reported as reasonably constant in a similar system.[2)]

Analyses of Products. The products were analyzed mainly by GLC without any treatment. The GLC analyses were performed on a Shimadzu GC-4BPTF with a 4.5 m× 3 mm column packed with 20% Silicone SE-30 on Uniport B. On occasion, GC-MS (GC: Hitachi M5201, column: Silicone OV-1 on Uniport KS, MS: Hitachi RMU-6MG) spectra were taken to identify the products. To obtain further information about the products, most of the catholytes were hydrolyzed by hydrochloric acid, and the aqueous solutions extracted with ether. The presence of lithium sulfide was examined by colorimetry using sodium pentacyanonitrosylferrate (III). Hydrogen sulfide and hydrogen gas were analyzed by GLC (Shimadzu GC-3AH with a 3 m×3 mm column packed with Silica gel 60—80 mesh).

Results and Discussion

Cyclic Voltammometry. The electrolytic decomposition of ethanol in HMPA solution is thought to be suppressed by the preferential adsorption of HMPA on the electrode surface.[2)] However, when the ethanol concentration becomes high, the ethanol decomposes, and the current efficiency for the generation of solvated electrons decreases. Therefore, in order to study the maximum alcohol concentration where the alcohol is not decomposed electrolytically, cyclic voltammograms were measured on the Pt electrode in 0.5 M lithium chloride–HMPA–ethanol solution with various ethanol concentrations, and the results are given in Fig. 1. The reduction waves at *approx.* −3.4 V *vs.* Ag/0.1 M Ag$^+$ are attributed to the generation of solvated electrons from the electrode, since the standard electrode potential of solvated electrons has been reported to be −3.4 V *vs.* Ag/0.1 M Ag$^+$ in HMPA,[12)] and the solutions turned dark blue where the ethanol concentrations were less than 50 mol %.[1,13,14)] When the ethanol concentration was increased up to 50 mol %, a further peak was observed at about −2.0 V. This peak became high in 67 mol % solution, and hydrogen gas evolved from the electrode surface in the potential region more negative than −1.5 V. This peak is apparently connected to the electrolytic decomposition of the ethanol.

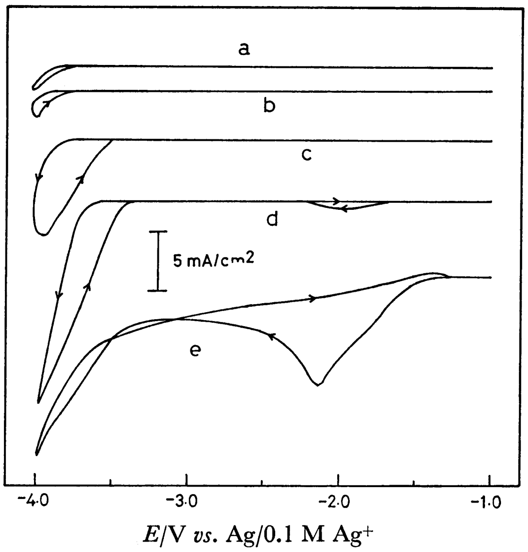


Fig. 1. Cyclic voltammograms on the Pt electrode in 0.5 M LiCl–HMPA–ethanol solutions. Ethanol concentration; a: 0, b: 14, c: 35, d: 50, and e: 67 mol %. Sweep rate: 3.3 mV/s.

On the basis of the above results, solutions with an alcohol concentration less than 50 mol % have been adopted for the following study. The detailed analysis of the cyclic voltammograms will appear in another report.

The cyclic voltammograms of solutions containing diphenyl sulfide gave the same pattern as in Fig. 1. Consequently, it was confirmed that no diphenyl sulfide was reduced electrolytically under the present experimental conditions.

Cleavage Reaction of Diphenyl Sulfide. Diphenyl sulfide was reduced by electrochemically generated solvated electrons. Tables 1 and 2 show the results in HMPA solutions with various ethanol concentrations and three types of 50 mol % alcohols, respectively. It should be remembered that in Table 2 the acidity of the alcohol, *i.e.*, the proton concentration in the solution decreased in the order, methanol > ethanol > 2-propanol, while the ease of α-hydrogen abstraction from the alcohol decreased in the reverse order.[15)] It was found from Tables 1 and 2 that benzene was formed as the main product indicating that the cleavage reaction proceeded in preference to the hydrogenation of the aromatic ring of diphenyl sulfide.

Several reports have appeared on the cleavage reaction of diphenyl sulfide by solvated electrons.[16,17)] Based on these reports, the following three reactions are possible for the present system:

$$\text{Ph–S–Ph} + e^-_{\text{solv}} \longrightarrow [\text{Ph–S–Ph}]^{\cdot -} \xrightarrow{e^-_{\text{solv}}} \text{Ph}^- + {}^-\text{S–Ph}, \qquad (1)$$

Table 1. Reduction products of diphenyl sulfide in HMPA–ethanol solutions

Ethanol concn, mol%	Yield of product, %						Conv.,[g)] %	Total current efficiency,[g)] %
	PhH[a)]	1,4-CHD[b)]	1,3-CHD[c)]	CHE[d)]	PhPh[e)]	Others[f)]		
50	32.7	10.3	1.6	1.3	tr	0.8	46.4	67.2
35	42.1	8.2	1.1	1.1	tr	3.2	54.3	69.6
14	65.1	0.0	0.0	0.0	1.8	0.0	66.9	61.4
0	84.8	0.0	0.0	0.0	1.8	2.4	88.9	79.4

a) Benzene. b) 1,4-Cyclohexadiene. c) 1,3-Cyclohexadiene. d) Cyclohexene. e) Biphenyl. f) Alkylbenzenes (toluene and ethylbenzene), alkyl phenyl sulfides (methyl phenyl sulfide and ethyl phenyl sulfide), and dibenzothiophene. g) 6 mmol of diphenyl sulfide was used. Quantity of electricity passed was 648 Q.

Table 2. Reduction products of diphenyl sulfide in HMPA–alcohol solutions

Alcohol[a]	Yield of product,[b] %						Conv.,[c] %	Total current efficiency,[c] %
	PhH	1,4-CHD	1,3-CHD	CHE	PhPh	Others		
MeOH	24.8	9.8	tr	1.6	tr	1.9	36.8	56.4
EtOH	32.7	10.3	1.6	1.3	tr	0.8	46.4	67.2
i-PrOH	59.6	3.9	tr	tr	0.4	0.7	64.4	64.8

a) Concentration was 50 mol %. b) Notations of products are the same as in Table 1. c) Obtained by the same conditions as in Table 1.

$$\text{Ph-S-Ph} + e^-_{\text{solv}} \longrightarrow [\text{Ph-S-Ph}]^{\overline{\cdot}} \longrightarrow \text{Ph}\cdot + {}^-\text{S-Ph} \qquad (2)$$

$$\text{Ph-S-Ph} + e^-_{\text{solv}} \longrightarrow [\text{Ph-S-Ph}]^{\overline{\cdot}} \longrightarrow \text{Ph}^- + \cdot\text{S-Ph} \qquad (3)$$

where e^-_{solv} denotes the solvated electron.

The results in Tables 1 and 2 indicate that the higher the ethanol concentration and acidity of the alcohol, the lower the conversion and benzene yield. These results imply that the protons in the solutions have no effect on the rate of benzene formation. Moreover, Table 2 shows that both the benzene yield and conversion depend on the ease of α-hydrogen emission of the alcohol. It can therefore be presumed that benzene is formed mainly according to Eq. 2, followed by hydrogen abstraction by the phenyl radical from the solvent,

$$\text{Ph}\cdot + \text{RH} \longrightarrow \text{PhH} + \text{R}\cdot \qquad (4)$$

where RH denotes the solvent (HMPA or alcohol). The detailed discussion of the further reaction of R· is beyond the scope of this paper.

Benzenethiol is expected *via* Eq. 2 as the pair product of benzene but remained undetected. It was detected quantitatively, however, after hydrolysis of the catholyte by hydrochloric acid. Since neither lithium sulfide nor hydrogen sulfide was detected in the products, the benzenethiolate formed by Eq. 2 is assumed to react with the lithium cation which is present in high concentration to produce lithium benzenethiolate.

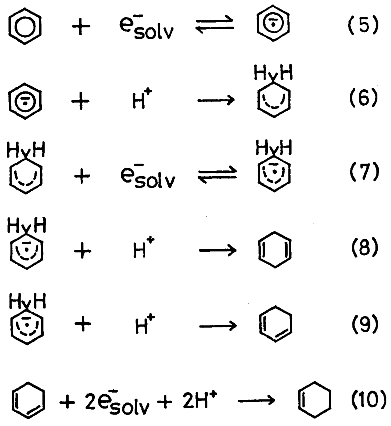
The formation of biphenyl, as minor products (Tables 1 and 2), is attributed to the coupling of the phenyl radicals and supports the validity of the reaction mechanism *via* Eq. 2. Cleavage of diphenyl sulfide was reported to proceed also by Eq. 2 when it was cleaved by potassium metal in liquid ammonia.[17]

Estimation of current efficiencies demonstrates almost conclusively that the cleavage reaction proceeds *via* the one-electron mechanism (Eq. 2), since the current efficiency for the formation of benzene estimated by the two-electron mechanism (Eq. 1) sometimes exceeds 100 % despite an ionic reaction without the existence of a radical chain reaction.

Hydrogenation Reaction of the Aromatic Ring. As shown in Table 1, 1,4- and 1,3-cyclohexadiene and cyclohexene were produced in 35 and 50 mol% ethanol–HMPA solutions. These products are believed to be formed by hydrogenation of the benzene, since no hydrogenated product of diphenyl sulfide without cleavage was detected. The ratio of hydrogenated products to benzene was high in 50 mol % ethanol solution compared with that in 35 mol %. Moreover, as may be seen from Table 2, the ratio increased depending on the acidity of the alcohol used. Therefore, the hydrogenation of the benzene is considered to be proton associated.

Krapcho and Bothner-By proposed a hydrogenation mechanism for benzene as shown in Scheme 1, which was obtained from alkali metal–liquid ammonia–alcohol systems.[18] The results in Tables 1 and 2 may be interpreted by this mechanism. The mechanism has also been supported by the hydrogenation of some unsaturated hydrocarbons in HMPA–alcohol solutions by electrochemically generated solvated electrons.[1–3] The rate determining step in this reaction is considered to be Eq. 6, since the availability of the hydroxyl proton of the alcohol will be rather low due to formation of a hydrogenated complex between alcohol and HMPA, in a manner similar to that for ethylenediamine solution,[19] and the hydrogenation was affected by the concentration and the acidity of the alcohol adopted. The same rate determining step was proposed by Krapcho and Bothner-By.[18]

According to the present mechanism, the production of one cyclohexadiene molecule from diphenyl sulfide requires three solvated electrons, *i.e.*, one for cleavage of diphenyl sulfide (Eq. 2) and two for hydrogenation of the benzene produced (Eqs. 5 and 7). Similarly, one cyclohexene molecule consumes five electrons. The total current efficiencies thus estimated are listed in Tables 1 and 2.



Scheme 1.

Effects of Current Density and Sulfide Concentration. Sternberg *et al.* proposed that the reduction rate of benzene by solvated electrons was proportional to benzene, solvated electron, and proton concentrations.[2] If a similar argument is applicable to the reduction of diphenyl sulfide, then the rate of cleavage of diphenyl sulfide is expected to increase when the concentration

TABLE 3. EFFECTS OF CURRENT DENSITY AND DIPHENYL SULFIDE CONCENTRATION ON REDUCTION OF DIPHENYL SULFIDE[a]

Current density, mA/cm^2	Diphenyl sulfide, mmol	Yield of product,[b] %					Conv.,[c] %	Total current efficiency,[c] %
		PhH	1,4-CHD	1,3-CHD	CHE	Others		
5[d]	6[d]	32.7 (29.4)	10.3 (27.6)	1.6 (4.3)	1.3 (5.8)	0.8	46.4	67.2
25	6	44.6	6.6	2.2	1.6	0.6	55.3	67.2
50	6	35.5	6.9	0.9	1.1	0.1	44.4	58.4
5	12	30.2 (54.2)	0.5 (2.7)	0.0 0.0	tr (tr)	0.9	31.0	57.2

a) Solution: 0.5 M LiCl–HMPA–50 mol % EtOH. b) Notations of products are the same as in Table 1. Current efficiency is shown in the parenthesis. c) Quantity of electricity passed was 648 Q. d) Usual conditions.

of diphenyl sulfide and the generation rate of solvated electrons (*i.e.*, current density) are raised. Therefore, to establish the most suitable reaction conditions for the reduction of diphenyl sulfide, the reactions were carried out at various current densities and diphenyl sulfide concentrations, the results of which are summarized in Table 3. The conversion and benzene yield increased as expected when the current density was raised from 5 to 25 mA/cm^2. On the contrary, when the current density was raised to 50 mA/cm^2, the total current efficiency, the conversion, and the yield of benzene derivatives decreased, and a large amount of hydrogen gas was evolved—the generation mechanism has been discussed by Sternberg *et al.*[2] It was found that a large increase in the current density such as 50 mA/cm^2 was not suitable for the reduction of diphenyl sulfide.

Doubling of the concentration of diphenyl sulfide produced a doubling of the current efficiency of benzene production (denoted in the parentheses in Table 3).

Reduction of Some Other Sulfides. In the case of diphenyl sulfide, the cleavage reaction proceeded preferentially compared to the hydrogenation under the present experimental conditions. This result, however, is not applicable to all sulfides having a phenyl group. Therefore, the reduction of some sulfides has been investigated in a similar manner, the results of which are given in Table 4 where the main products and current efficiencies are summarized. Products obtained after hydrolysis are designated in parentheses.

TABLE 4. REDUCTION PRODUCTS OF SOME SULFIDES IN HMPA SOLUTIONS

Reactant	Hexyl phenyl sulfide		Benzo[*b*]-thiophene		Dibenzo-thiophene		Tetra-hydro-thiophene	
Ethanol concn, mol %	0	50	0	50	0	50	0	50
Current efficiency of main product, %	n-C_6H_{14} 55.5	39.0	3,4-Dihydrobenzo[*b*]-thiophene 0.0	53.8	2H-[a] 0.0	3.6	n-BuSH 45.5	3.7
	n-$C_{12}H_{26}$ 21.2	3.2			4H-[b] 0.0	7.6	$(n\text{-Bu})_2S$ 10.2	4.8
	n-C_6H_{12} 2.8	0.0					n-BuSEt 0.0	4.2
	PhH 0.7	0.4						
	(PhSH)[c]							
Total current efficiency, %	80.2	42.6	0.0	53.8	0.0	11.2	55.7	12.7

a) Dihydro product. b) Tetrahydro product.
c) Detected after hydrolysis.

Hexyl phenyl sulfide underwent cleavage in a similar manner to diphenyl sulfide, that is, the reduction was not accelerated in the presence of ethanol and benzenethiol was detected quantitatively after hydrolysis of the catholyte. The formation of hexane and the coupling of hexyl radicals as the main products suggests that β-cleavage took place predominantly (Eq. 11). The course

$$C_6H_{13}\overset{\beta}{-}S\overset{\alpha}{-}Ph \xrightarrow{e^-_{solv}} C_6H_{13}\cdot + {}^-S\text{–}Ph \tag{11}$$

of cleavage of aryl decyl ethers by alkali metals was investigated in HMPA–THF solvents by Itoh *et al.* where it was suggested that highly polar solvents and small alkali metals favor β-cleavage.[6] This suggestion is supported here.

In the case of benzo[*b*]thiophene and dibenzothiophene, only the hydrogenated products were obtained in 50 mol % ethanol–HMPA solution and in HMPA solution without ethanol, no reaction occurred. The C–S bonds of these sulfides are considered to be more stable than those of the alkyl phenyl and diphenyl sulfides. It has been reported that the hydrogenation of dibenzothiophene proceeds in preference to the cleavage of C–S bonds when reduced in ethylenediamine by

TABLE 5. REDUCTION PRODUCTS OF SOME ETHERS IN HMPA SOLUTIONS

Reactant	Diphenyl ether		Isobenzo-furan		Dibenzo-furan		Tetrahydro-furan	
Ethanol concn, mol %	0	50	0	50	0	50	0	50
Current efficiency of main product,[a] %	PhH 41.5	43.7	3,4-dihydro-benzo-furan 0.0	61.4	2H- 0.0	1.6	n-BuOH 0.0	11.5
	1,4-CHD 0.0	1.7			4H- 0.0	2.2	n-BuOEt 0.0	8.8
	CHE 0.0	1.1					n-C_4H_{10} tr	0.0
	(PhOH)							
Total current efficiency, %	41.5	46.5	0.0	61.4	0.0	3.8	tr	20.3

a) Notations of products are the same as in Tables 1 and 4.

electrochemically generated solvated electrons, and that no sulfur was eliminated until partial hydrogenation of the aromatic ring had taken place.[20]

The reduction of tetrahydrothiophene was attempted to establish whether the cyclic sulfide can be cleaved by the present method. This compound was selected because it was considered the simplest representative of the completely hydrogenated thiophenes. As shown in Table 4, tetrahydrothiophene cleaved, although the current efficiencies were relatively low compared with those of the diphenyl and hexyl phenyl sulfides.

Reduction of Some Ethers. The reduction of some ethers was conducted to compare the behavior with that of the sulfides. The results in Table 5 show that the ethers were reduced in the same way as the corresponding sulfides. In the case of tetrahydrofuran in HMPA solution without ethanol, the high resistivity of the solution caused no appreciable reaction.

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References

1) H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Am. Chem. Soc.*, **89**, 186 (1967).

2) H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Am. Chem. Soc.*, **91**, 4191 (1969).

3) T. Asahara, M. Seno, and H. Kaneko, *Bull. Chem. Soc. Jpn.*, **41**, 2985 (1968).

4) T. Asahara, M. Seno, T. Ibuki, and H. Asagahara, *Yukagaku*, **22**, 27 (1973).

5) L. A. Avaca and A. Bewick, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1709.

6) M. Itoh, S. Yoshida, T. Ando, and N. Miyaura, *Chem., Lett.*, **1976**, 271.

7) L. Reggel, R. Raymond, S. Friedman, R. A. Friedel, and I. Wender, *Fuel*, **37**, 126 (1968).

8) H. W. Sternberg and C. L. D. Donne, *Fuel*, **53**, 172 (1974).

9) M. Nakazaki, "Yūkikagōbutsu Gōseihō," Gihōdō, Tokyo (1966), Vol. 8.

10) D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd ed, McGraw-Hill, New York (1964), p. 253.

11) "Bunseki-kagaku Jikken," ed by Y. Uzumasa, Kagaku-dōzin, Kyoto (1965), p. 183.

12) Y. Kanzaki and S. Aoyagui, *J. Electroanal. Chem.*, **36**, 297 (1972).

13) J. M. Brooks and R. R. Dewald, *J. Phys. Chem.*, **72**, 2655 (1968).

14) R. Catterall, L. P. Stodulski, and M. C. Symons, *J. Chem. Soc., Inorg.*, **1968**, 437.

15) W. E. Truce and J. J. Breiter, *J. Am. Chem. Soc.*, **84**, 1621 (1962).

16) R. Gerdil and E. A. C. Lucken, *J. Chem. Soc.*, **1963**, 5444.

17) R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.*, **96**, 112, (1974).

18) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

19) J. R. Brandon and L. M. Dorfman, *J. Chem. Phys.*, **53**, 3849 (1970).

20) H. W. Sternberg, C. L. D. Donne, and I. Wender, *Fuel*, **47**, 219 (1968).