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Potentiometric and Spectrophotometric Studies of Nickel(II)–Nitrate Complexes in Molten Dimethyl Sulfone and in the Molten $LiNO_3$–$NaNO_3$–KNO_3 Eutectic[1a]

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Nickel(II) was shown potentiometrically to form successive 1:2 and 1:3 complexes with nitrate in dimethyl sulfone at 125°, and values of the formation constants were determined. An amalgamated nickel coil served as the indicator electrode, and the silver(I)–silver system was used as the reference electrode. These potentiometric results were confirmed by spectrophotometric measurements, and the ligand field spectra of the nickel(II) species involved were determined. The spectrum of nickel(II) in the molten $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 125° was measured and found to correspond closely to that of the 1:3 complex.

Introduction

Molten nitrates have been widely used as solvents in electrochemical and spectrophotometric investigations.[2,3] In these media nickel(II) is coordinated to nitrate oxygens with a more or less octahedral geometry[4] but the structure and composition of the complex have not been identified. As an initial step toward determining the complex in nitrate salt melts, we studied the formation of successive nickel(II)–nitrate complexes in molten dimethyl sulfone at 125° by potentiometric and spectrophotometric methods and measured the nickel(II) spectrum in the molten $LiNO_3$–$NaNO_3$–KNO_3 eutectic at the same temperature. The results, reported here, show the formation of 1:2 and 1:3 complexes in molten dimethyl sulfone and the near-identity of the spectrum of the complex in the nitrate salt eutectic with that of the 1:3 complex.

Experimental Section

Chemicals. Dimethyl Sulfone.—Commercial reagent was recrystallized once from water and three times from methanol and then vacuum dried.

Lithium Perchlorate.—Perchloric acid was allowed to react with lithium carbonate to yield the hydrated salt which was then dried in the molten state at 240°. A detailed preparative procedure is given elsewhere.[5]

Silver Perchlorate.—Perchloric acid was slowly added to silver carbonate. After filtration, the solution was evaporated to dryness, and the white product was dried at 170°.

Nickel Perchlorate Hexahydrate.—Perchloric acid was slowly added to excess nickel carbonate. After filtration, the solution was evaporated until it appeared saturated. The green needles, which separated upon cooling, were filtered out and stored while moist in a desiccator over anhydrous calcium sulfate, which does not remove the water of hydration.

Nickel Nitrate Hexahydrate.—Commercial reagent was twice recrystallized from water.

Lithium Nitrate.—Commercial reagent was twice recrystallized from water and dried at 150°.

Nickel Perchlorate and Nitrate Solutions in Dimethyl Sulfone.—A weighed amount of the hydrated nickel salt was added to a desired amount of dimethyl sulfone. The mixture was heated to 130–150°, and dry argon or nitrogen was passed vigorously through the solution overnight. After the flushing was completed, the solution was brought to volume with enough dimethyl sulfone and lithium perchlorate to give the desired concentration of nickel(II). Analysis indicated a water content less than 0.01% in these preparations. In several cases, the nickel contents were analyzed to confirm the calculated concentrations.

Potentiometric Measurements.—In these measurements, a silver perchlorate–silver reference electrode and an amalgamated nickel wire indicator electrode were used. The suitability of these electrodes in dimethyl sulfone has already been demonstrated.[5] Individual electrode compartments were separated from the main bath by sintered-glass frits, which also served as salt bridges. Lithium perchlorate at a concentration of 2 *M* was used as the inert electrolyte. The volume of the solution in each compartment was calculated from weight and density data. Silver(I) was added to the reference electrode compartment either as silver perchlorate or by coulometric generation. In some cases, the nickel perchlorate solution in dimethyl sulfone, previously described, was used in the sample compartment; nickel(II) could also be generated coulometrically. The potential of an amalgamated nickel indicator electrode in the nickel(II) solution was measured against the silver reference electrode. Lithium nitrate was then added in successive weighed portions, and the potential measurement was repeated after each addition. A detailed description of the experimental setup and procedure is given elsewhere.[5]

Spectrophotometric Measurements.—The spectra were obtained on a Cary Model 14H spectrophotometer with a furnace which has been described elsewhere.[6] Square silica cells with a 1-cm path length were used. The absorption curves of the solvent media and the solutions of interest were measured against air as reference, and the absorbances of the solutions were obtained by difference.

A weighed amount of dimethyl sulfone solution of nickel perchlorate or nickel nitrate in 3 *M* lithium perchlorate was placed in a cell, and the absorption curve was measured. Successive weighed portions of lithium nitrate were added to the solution, and the spectral measurement was repeated after each addition. The volumes of the solutions were calculated from their total weights and densities. The latter were determined by the float method.[7] The molar concentrations of nickel(II) ranged from 0.01 to 0.07 *M*, and the highest nitrate concentration examined was 1.5 *M*. In separate experiments, the absorption spectra of solutions of similar compositions, except for the absence of nickel(II), were measured.

Nickel(II) solutions in the $LiNO_3$–KNO_3–$NaNO_3$ eutectic were

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[2] C. H. Liu, K. E. Johnson, and H. A. Laitinen in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, pp 681–733.

[3] G. P. Smith in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, pp 427–503.

[4] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

[5] C. H. Liu, L. Newman, and J. Hasson, to be submitted for publication.

[6] C. R. Boston and G. P. Smith, *Rev. Sci. Instr.*, **36**, 206 (1965).

[7] C. R. Boston, *J. Chem. Eng. Data*, **11**, 262 (1965).

prepared by adding anhydrous nickel sulfate to the solvent nitrates. The concentration of nickel was determined from the weights of the components and the density of the eutectic. The density was measured with a platinum sinker and found to be $\rho = 2.086 - (7.53 \times 10^{-4}t)$, where ρ is the density in grams per cubic centimeter and t is the temperature in degrees centigrade.

The spectrum of nickel(II) in the nitrate melt was measured by the same procedure used for the solutions in molten dimethyl sulfone.

Results and Discussion

Analysis of the potentiometric results by Leden's method[8] indicates that the ratio 1:2 and 1:3 nickel(II)-nitrate complexes were the only ones formed.

We present the experimental data in the following manner: If nickel(II) forms only two complexes, the successive formation constants, K_2 and K_3, can be written in terms of the equilibrium concentrations, represented by brackets; thus

$$K_2 = \frac{[\mathrm{Ni(NO_3)_2}]}{[\mathrm{Ni^{2+}}][\mathrm{NO_3^-}]^2} \qquad (1)$$

$$K_3 = \frac{[\mathrm{Ni(NO_3)_3^-}]}{[\mathrm{Ni(NO_3)_2}][\mathrm{NO_3^-}]} \qquad (2)$$

It can be shown that

$$K_2 + K_2K_3[\mathrm{NO_3^-}] = \frac{I - 1}{[\mathrm{NO_3^-}]^2} \qquad (3)$$

where I = antilog $(-\Delta E/0.0395)$, $\Delta E = E_c - E_s$, and E_c and E_s are the potentials of the complex and simple ions, respectively, at the same total nickel(II) concentration. Thus, if $[\mathrm{NO_3^-}]$ is plotted against $(I - 1)/[\mathrm{NO_3^-}]^2$, a straight line should result. The intercept should be equal to K_2 and the slope to K_2K_3. A set of representative experimental results is presented in Figure 1. The plot is a straight line, and K_2 and K_3 are found to be 2.7×10^3 and 6.0, respectively.

Spectrophotometrically, it was found that solutions of $\mathrm{Ni(BF_4)_2 \cdot 8H_2O}$ and $\mathrm{Ni(ClO_4)_2 \cdot 6H_2O}$ dehydrated *in situ* in dimethyl sulfone at 125° gave identical nickel(II) ligand field bands. The addition of $\mathrm{LiBF_4}$ or $\mathrm{LiClO_4}$ produced no changes in these bands. It is reasonable, therefore, to suppose that the spectrum obtained was that of nickel(II) coordinated with solvent molecules. Successive additions of lithium nitrate produced pronounced changes in the spectrum. Figure 2 presents the spectra of nickel(II) solutions at various lithium nitrate concentrations. Since $\mathrm{Ni(NO_3)_3^-}$ is relatively unstable in dimethyl sulfone, a limiting spectrum was not reached even when the solution was saturated with $\mathrm{LiNO_3}$.

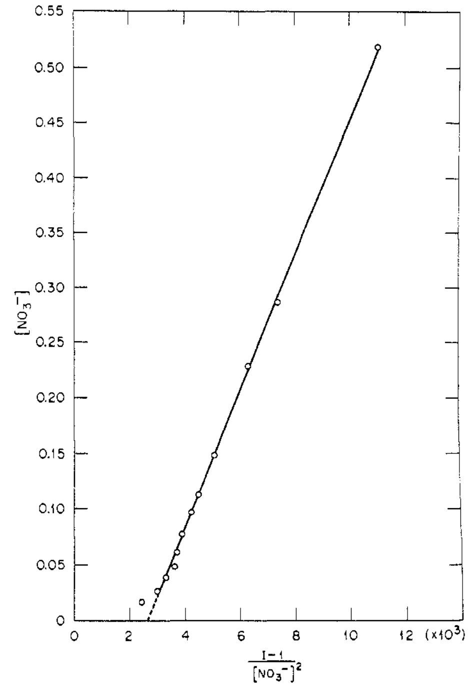

Figure 1.—Potentiometric evaluation of formation constants for the case in which $C_{\mathrm{Ni}} = 8 \times 10^{-4}$ *M*.

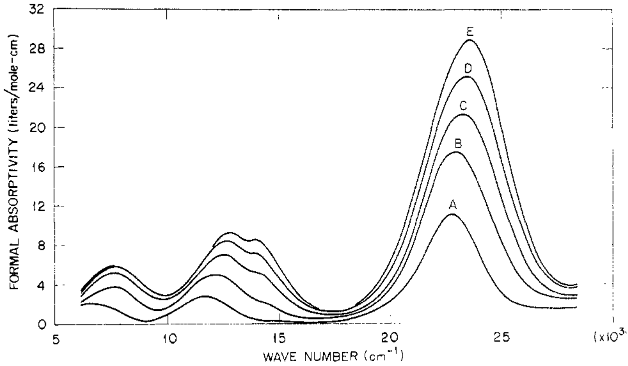

Figure 2.—Spectra of nickel(II) in molten dimethyl sulfone at various nitrate concentrations. Values of C_{Ni} and $C_{\mathrm{NO_3}}$, respectively, are as follows: A, 0.0334 and 0; B, 0.0334 and 0.0292; C, 0.0672 and 0.134; D, 0.0668 and 0.268; E, 0.0651 and 0.875.

The spectra of the complexes $\mathrm{Ni(NO_3)_3^-}$ and $\mathrm{Ni(NO_3)_2}$ were obtained in the following manner. Based upon the potentiometrically determined formation constants, less than 0.5% of the nickel(II) is present as the simple ion at equilibrium nitrate concentrations greater than about 0.2 *M*, and $\mathrm{Ni(NO_3)_3^-}$ and $\mathrm{Ni(NO_3)_2}$ are the only significant nickel-containing species present. The existence of this two-species equilibrium was confirmed by plots of the formal absorptivities, A/C_{Ni}, at two different wave numbers against each other at various nitrate concentrations; A is the absorbance of the solution in a cell of 1-cm path length at a given wave number, and C_{Ni} is the total nickel(II) concentration. Typical linear plots are shown on Figure 3. Under the condition of this two-species equilibrium, it can be shown that

$$A/C_{\mathrm{Ni}} = \epsilon_2 + (\epsilon_3 - (A/C_{\mathrm{Ni}}))[\mathrm{NO_3^-}]K_3 \qquad (4)$$

where ϵ_2 and ϵ_3 are the molar absorptivities of $\mathrm{Ni(NO_3)_2}$ and $\mathrm{Ni(NO_3)_3^-}$, respectively, at the same wave number. At each wave number chosen, if the correct ϵ_3 is used, a plot of A/C_{Ni} *vs.* $(\epsilon_3 - (A/C_{\mathrm{Ni}}))[\mathrm{NO_3^-}]$ should result in a straight line with a slope equal to K_3 and an intercept equal to ϵ_2. An erroneous choice of ϵ_3 is reflected as a positive or negative deviation from linearity. Figure 4 shows a typical plot at 23,810 cm^{-1}. Similar plots were made at 14,085 and 12,903 cm^{-1}, and K_3 was evaluated to be 3.5 ± 1.0. The values of ϵ_2 and ϵ_3 at these wave numbers were also de-

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[8] I. Leden, *Z. Physik. Chem.*, **188**, 160 (1941).

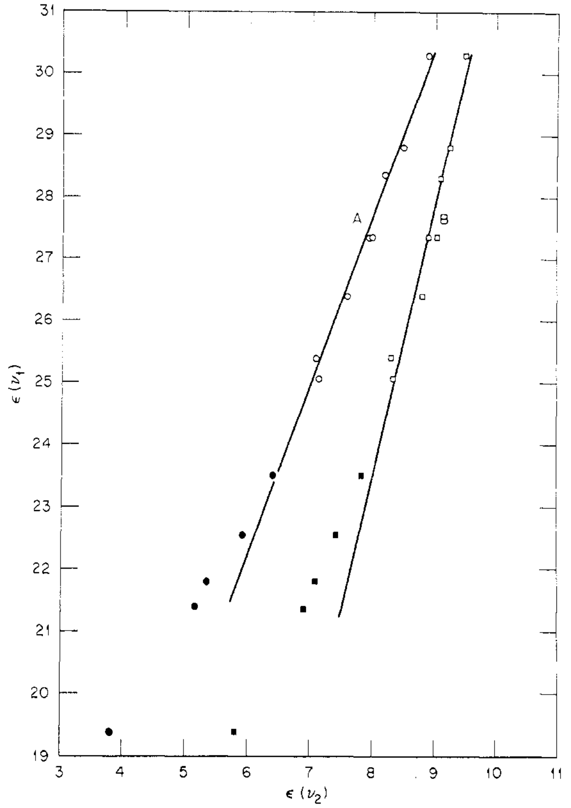

Figure 3.—Confirmation of two-species equilibrium: A, ε at 23,620 cm^{-1} *vs.* ε at 13,900 cm^{-1}; B, ε at 23,620 cm^{-1} *vs.* ε at 12,820 cm^{-1}. Solid points represent data for spectra at [NO$_3^-$] less than 0.12 *M*.

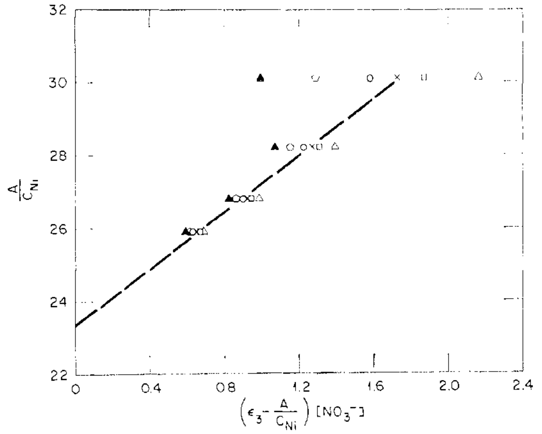

Figure 4.—Plot of $A/C_{\rm Ni}$ *vs.* $(\epsilon_3 - (A/C_{\rm Ni}))[{\rm NO_3^-}]$ at various ϵ_3 values: ▲, 30.8; ◯, 31.0; ○, 31.2; ×, 31.3; □, 31.4; △, 31.6.

termined. It can be shown that if $Ni(NO_3)_3^-$ and $Ni(NO_3)_2$ are the only light-absorbing species at equilibrium, the formal absorptivity of a dilute nickel(II) solution at a particular equilibrium nitrate concentration is given by a linear combination of ϵ_2 and ϵ_3, namely

$$A/C_{\rm Ni} = x\epsilon_2 + (1 - x)\epsilon_3 \tag{5}$$

where x is the fraction of nickel(II) present as $Ni(NO_3)_2$. Since ϵ_2 and ϵ_3 have been determined at several wave numbers, a unique value of x can be calculated for each spectrum. A combination of two spectra at two different nitrate concentrations then yields the pure spectra of $Ni(NO_3)_2$ and $Ni(NO_3)_3^-$. These spectra are presented in Figure 5 along with the spectrum of nickel(II) in the molten $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 125°.

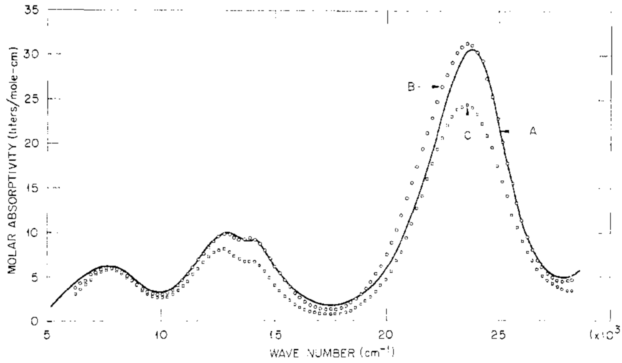

Figure 5.—Spectra of nickel(II)–nitrate species: A (solid line), nickel(II) in the molten $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 125°; B (circles), $Ni(NO_3)_3^-$ in molten dimethyl sulfone at 125°; C (squares), $Ni(NO_3)_2$ in molten dimethyl sulfone at 125°.

In evaluating K_2, spectrophotometric measurements of the concentrations of the nickel(II) species do not yield precise results since the low equilibrium nitrate concentration, which is measured by difference between the total nitrate concentration and the nitrate consumed in complexation, cannot be determined with precision. Furthermore, severe overlapping of the nitrate bands in the uv region by the bands of the nickel(II) complex prevents a direct spectrophotometric determination of the nitrate concentration. At high nitrate concentrations, the simple nickel(II) concentration becomes very small, and precision in its spectrophotometric evaluation is again lost. The most favorable conditions under the circumstances are achieved when the nitrate concentration is sufficiently high so that it can be measured by difference with reasonable precision but sufficiently low so that the simple nickel(II) concentration is appreciable. In this nitrate concentration range, it can be shown that

$$[{\rm Ni(NO_3)_2}] = \frac{A - A_0}{(\epsilon_2 - \epsilon_0) + K_3(\epsilon_3 - \epsilon_0)[{\rm NO_3^-}]} \tag{6}$$

where ϵ_0 is the absorptivity of the simple nickel(II) ion, A is the absorbance of the solution, and A_0 is the absorbance of the solution in the absence of nitrate. Also

$$[{\rm Ni(NO_3)_3^-}] = K_3[{\rm NO_3^-}][{\rm Ni(NO_3)_2}] \tag{7}$$

$$[{\rm NO_3^-}] = C_{\rm NO_3} - 2[{\rm Ni(NO_3)_2}] - 3[{\rm Ni(NO_3)_3^-}] \tag{8}$$

where $C_{\rm NO_3}$ is the total nitrate concentration, and

$$[{\rm Ni^{2+}}] = C_{\rm Ni} - [{\rm Ni(NO_3)_2}] - [{\rm Ni(NO_3)_3^-}] \tag{9}$$

In a solution of known $C_{\rm NO_3}$, the values of $[Ni(NO_3)_2]$, $[Ni(NO_3)_3^-]$, and $[NO_3^-]$ can be evaluated by successive approximation from eq 6–8, and $[Ni^{2+}]$ is obtained in turn from eq 9. Then K_2 can be calculated. In the $C_{\rm Ni}$ range 0.0334–0.0672 *M* and the $[NO_3^-]$ range 0.014–0.075 *M*, K_2 was evaluated to be (3.6 ± 1.3) × 10^3 in seven determinations at each of three wave numbers (23,810, 14,085, and 12,903 cm^{-1}). In view of the complexity of the system, the inherent experimental difficulties, and the differences in ionic strengths, we regard the spectrophotometric values of the successive formation constants as being in satisfactory agreement.

All three spectra shown in Figure 5 clearly belong to species with more or less octahedral coordination. All three spin-allowed bands are present, and the shoulder on the high-energy side of the middle band is plausibly assigned to the $^3A_2 \rightarrow {}^1E$ transition intensified by singlet–triplet mixing. It will be seen from Figure 5 that the spectrum of nickel(II) in the molten $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 125° is strikingly similar to that of the $Ni(NO_3)_3^-$ complex in molten dimethyl sulfone at the same temperature. Thus we suppose that the same entities are present in both media. Since nickel(II) can only be complexed to NO_3^- in the nitrate melt, we conclude that nitrate behaves as a bidentate ligand in a distorted octahedral structure. Also, we suppose that the two nitrate ions in the dinitrato complex may act either as bidentate ligands and occupy planar positions or as unidentate ligands and occupy pyramidal positions. (Attempts are being made to prepare the dinitrato and trinitrato complexes in solid form for X-ray structure determinations.)

Although the coordination of nickel(II) in the $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 125° appears to have a well-defined geometry, it is by no means certain that such regularity persists up to significantly higher temperatures. A progressive broadening of the distribution of coordination geometries with increasing temperature, such as occurs in chloride systems,[9] almost certainly will also occur in molten nitrates. The only question is whether or not this broadening becomes significant at temperatures below those at which the melt decomposes.

The compound methyltriphenylarsonium tetranitratonickelate(II) has been reported in the literature.[10] Although the data presented here do not eliminate entirely the possibility that the entity in the melt is the 1:4 complex, a published spectrum,[10] presumed to be that of the 1:4 complex, is substantially different from the melt spectrum presented here.

[9] J. Brynestad, C. R. Boston, and G. P. Smith, *J. Chem. Phys.*, **47**, 3179 (1967); and J. Brynestad and G. P. Smith, *ibid.*, **47**, 3190 (1967).

[10] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

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Reactions between Sodium Carboxylic Acid Salts and Molten Sodium Nitrate and Sodium Nitrite

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The over-all reactions of NaCOOH and $NaC_2H_3O_2$ in $NaNO_3$ and $NaNO_2$ have been examined using infrared analysis, cryoscopy, voltammetry, and chronopotentiometry. The over-all reactions with NaCOOH are

$$NaCOOH + NaNO_3 \longrightarrow NaNO_2 + {}^1/_2Na_2CO_3 + {}^1/_2H_2O + {}^1/_2CO_2$$

and

$$NaCOOH + NaNO_2 \longrightarrow Na_2CO_3 + {}^1/_2N_2O + {}^1/_2H_2O$$

Similarly with $NaC_2H_3O_2$ the reactions are

$$NaC_2H_3O_2 + 4NaNO_3 \longrightarrow {}^1/_2Na_2CO_3 + {}^3/_2H_2O + 4NaNO_2$$

and

$$NaC_2H_3O_2 + 3NaNO_2 \longrightarrow 2Na_2CO_3 + {}^3/_2H_2O + {}^1/_2N_2O + N_2$$

The reactions with NaCOOH were much more rapid than the reactions with $NaC_2H_3O_2$ in $NaNO_3$ at approximately 320°. The need for caution in examining these systems is stressed because of the danger of explosions at high concentrations of carboxylic acid salts. Equations are proposed for the reaction of $NaC_3H_5O_2$ with $NaNO_3$ by generalizing from the reaction schemes given for formate and acetate. The predicted values for the number of cryoscopic species generated in $NaNO_3$ agreed well with those experimentally found in the same system.

Introduction

Reactions between molten salts and organic materials have been of interest because of the potential of such systems for producing useful organic and metalloorganic compounds. Sundermeyer[1] has reviewed such systems. More recent work has also considered the use of molten nitrates for synthesizing nitrobenzenes.[2] Studies of simpler species, such as carboxylic acid salts in inorganic nitrate melts, have also been reported. Thus Guenther[3] demonstrated the ability of sodium

[1] W. Sundermeyer, *Angew. Chem. Intern. Ed. Engl.*, **4**, 222 (1965).

[2] R. B. Temple, C. Fay, and J. Williamson, *Chem. Commun.*, 966 (1967).

[3] K. F. Guenther, *J. Phys. Chem.*, **67**, 2851 (1963).