

### Discussion

The results of this study confirm that barium pernitride results from the thermal decomposition of the azides under a liquid phase. The exact composition of the pure compound is still unknown, but the substance appears to be either nonstoichiometric  $Ba_3N_4$  or mixtures of  $Ba_3N_4$  with the orthonitride ( $Ba_3N_2$ ), both in a microcrystalline state. There is insufficient evidence to confirm beyond doubt the ideal formula often quoted,  $Ba_3N_4$ .

Contrary to earlier reports, the hydrocarbon under which the  $Ba(N_3)_2$  decomposes is seriously degraded, evidently resulting in  $BaH_2$  and  $Ba(HC_2)_2$  (and possibly  $BaC_2$ ), along with some elemental carbon. The presence of these substances is revealed by the composition of the gases formed on hydrolysis. The acetylides generally constitute an estimated 3–5% of the total solids. The two proton nmr lines observed by Linke and Lingmann<sup>3b</sup> might be ascribable to  $Ba(HC_2)_2$  and  $BaH_2$ . Even the normally inert halocarbons are degraded when heated with barium azide, Fluorolube to  $BaF_2$  and  $BaCl_2$ , and decafluorobiphenyl to  $BaF_2$ ; barium acetylide and carbon are formed as well. Mineral oil is attacked when heated at 280° with sodium azide; hydrolysis of the resulting mixture yields no nitrogen, but acetylene, along with some hydrogen. Pernitrides of barium, strontium, and calcium only are known.

Linke, *et al.*,<sup>3d</sup> reported a temperature-dependent paramagnetism of  $Ba_3N_4$  using the Gouy method. The result is in direct conflict with the observations in the present study by esr, that  $Ba_3N_4$  is not paramagnetic from room temperature to 250° and that no paramagnetic intermediates are detected during its formation.

It is by no means clear how the liquid phase changes the manner of decomposition of barium azide. There is an extensive literature on the thermal and photolytic decomposition of alkaline earth azides.<sup>7,8</sup> Insufficient studies are available to draw a detailed picture, but an approximate course of events is as follows. On heating dry barium azide, nuclei appear on the crystal surfaces and grow as the net reaction  $4Ba(N_3)_2 \rightarrow Ba_3N_2 + Ba + 11N_2$  occurs.<sup>5c-f</sup> Neutral  $N_3$  radicals might be an intermediate.<sup>8</sup> Esr studies of barium azide irradiated with ultraviolet indicate<sup>8</sup> formation of the  $N_2^-$  molecule ion, which can be further converted reversibly to  $N_2$  by electron transfer:  $N_2^- + N_3^- \rightleftharpoons N_2 + N_3^{2-}$ . The molecule ion is thus believed to be the precursor of elemental nitrogen. Esr studies of  $Ba(N_3)_2$  irradiated with X-rays at 77°K<sup>8h</sup> also show  $N_3^{2-}$  and in addition a species which is evidently a paramagnetic, neutral nitrogen atom. Photodecomposition of aqueous solutions of barium azide yield nitrogen, ammonia, hydrazine, and hydroxylamine.<sup>5a</sup>

But when crystals of the azide are covered with a relatively inert liquid and the temperature raised to 140–200°, the course of the reaction is changed dramatically. The liquid is evidently adsorbed at the sites of decomposition nuclei, and quenches or arrests complete decomposition to the orthonitride. Since no paramagnetic intermediate could be detected during the course of decomposition of barium azide

to the pernitride under mineral oil, the  $N_2^-$ ,  $N_3^{2-}$ , or N radicals which are reported to result by irradiation either are not formed or do not persist long enough for detection at the elevated temperatures.

The formation of barium amalgam when the azide is decomposed could readily result from the dissolution of nascent metal by mercury. When the pernitride preparation is treated with liquid ammonia, no trace of the intense blue color (ammoniated electron) which would result were metallic barium present is observed, and there is no initial gas evolution.

Since crystallographic, infrared, and esr studies yield little useful information concerning these intractable substances, it might well be that solid-state broad-line <sup>14</sup>N nmr or better, multipulse nmr techniques<sup>9</sup> using <sup>15</sup>N-enriched samples would be able to distinguish any  $N_2$  or  $N_4$  groups or even more highly polymerized units of nitrogen atoms. Electron spectroscopy of the 1s shell (ESCA) of nitrogen and barium would reveal any nonequivalency in these types of atoms. There might also be a difference in behavior between the anhydrous barium azide which crystallizes out of aqueous solution above 52.5°<sup>10</sup> and the material usually made by dehydrating the monohydrate, which is obtained below this temperature.

Registry No.  $Ba_3N_4$ , 12047-80-2;  $Ba(N_3)_2$ , 18810-58-7.

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Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201

### Carbon Monosulfide Used in Synthesis of Halosulfur Compounds

Kenneth J. Klabunde,\* Curt M. White, and Howard F. Efner

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Relatively little is known about the general chemical properties and uses of carbon monosulfide (CS). This reactive molecule has been observed in significant amounts in the upper atmosphere<sup>1</sup> and as an intermediate in the photolysis and combustion of carbon disulfide ( $CS_2$ ).<sup>2</sup> Numerous spectroscopic studies have been reported for CS.<sup>3–9</sup> However, only Steudel<sup>5,8,9</sup> has reported results where CS has

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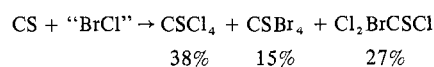
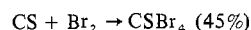
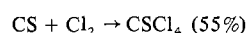
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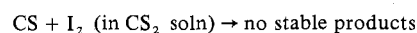
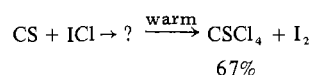
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been used as a synthetic intermediate, but only on small scale with relatively few reagents. Verkade and coworkers very recently used a small-scale CS-Ni atom reaction to produce apparently unstable Ni(CS)<sub>4</sub>.<sup>10</sup>

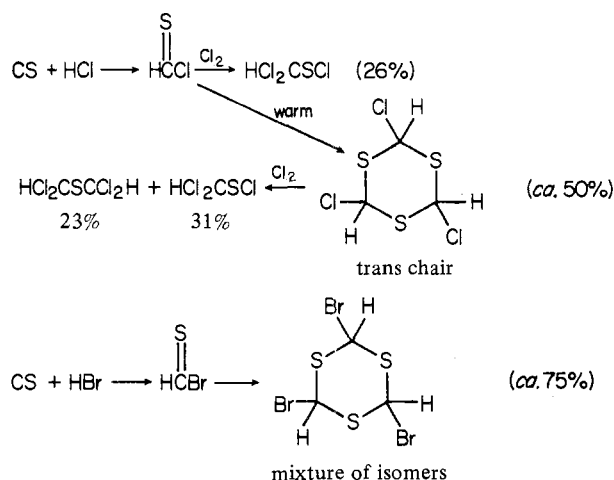
We have produced CS in several gram quantities employing a modified high-voltage ac discharge<sup>7</sup> through CS<sub>2</sub> in a vacuum flow system. Our interest has been in using CS as a synthetic reagent at low temperatures, and we have carried out both cocondensation experiments (-196°) and low-temperature solution experiments. Thus, we have condensed CS with excesses of halogens and mixed halogens to prepare CSX<sub>4</sub> compounds: trichloromethanesulfonyl chloride (CSCl<sub>4</sub>), tribromomethanesulfonyl bromide (CSBr<sub>4</sub>), and bromodichloromethanesulfonyl chloride (BrCl<sub>2</sub>CSCl). Unfortunately, iodo derivatives could not be prepared this way due to appar-



ently facile halogen exchanges or simply poor stability.



Although two molecules of Cl<sub>2</sub> or Br<sub>2</sub> readily add to CS, HCl and HBr only add once. Using these hydrogen halide reactions we have generated the thioformyl halides (HXC=S), to our knowledge previously unknown. These thioformyl halides trimerized readily when the cold reactor was allowed to warm slowly to room temperature. If a small amount of Cl<sub>2</sub> was present during the CS-HCl codeposition, the HClC=S was trapped to form dichloromethanesulfonyl chloride (HCl<sub>2</sub>CSCl). However, methanol trapping was not



successful under these conditions. Addition of Cl<sub>2</sub> to the HClC=S trimer (2,4,6-trichloro-1,3,5-trithiane) yielded cleavage products bis(dichloromethyl) sulfide (HCl<sub>2</sub>CSCCl<sub>2</sub>H) and HCl<sub>2</sub>CSCl, the same products obtained from chlorination of 1,3,5-trithiane itself.<sup>11</sup>

The 2,4,6-trihalo-1,3,5-trithianes are heavy oils that are sensitive to air, especially the bromo derivative. An nmr

study of these trimers was quite interesting. Apparently only one geometrical isomer of the thioformyl chloride trimer was formed, indicated by two of the three hydrogens being equivalent. Nmr (CS<sub>2</sub>): singlets at δ 6.73 (1 H) and 6.29 (2 H). This spectrum would be expected for a non-rapidly inverting trans chair structure.<sup>12,13</sup> However, for the thioformyl bromide trimer apparently both the cis (all hydrogens axial, least sterically hindered isomer) and the trans (two hydrogens axial) chair structures were formed. Nmr (CS<sub>2</sub>): singlets at δ 6.82 (2 H), 6.55 (ca. 1.2 H), and 6.47 (1 H). The peak at δ 6.55 is apparently due to the cis isomer and shows that a small amount of it was formed. Unfortunately the sensitive and reactive nature of this material did not allow isomer separation by column chromatography. In perdeuteriobenzene the trimers showed very large chemical shift changes and a merging of the singlets, which is characteristic of the formation of collision complexes with the benzene π system, as previously observed for *m*-dioxanes and similar systems<sup>14</sup> (see Table I for complete nmr data).

During our investigation we have made a number of observations that may be of use to other workers. First, an ac discharge is a very satisfactory source of CS for synthetic uses. Sulfur plates out rapidly in the discharge tube while the CS can be moved a good distance (>5 m) in the gas phase (confirming the report by Dyne and Ramsay<sup>3</sup>). The CS monomer can be coated on any cold (<-160°) surface, and on warming a brown-black CS polymer forms which adheres tenaciously to metal and glass. This CS polymer is very inert chemically and will slowly decompose at 150° in an air or nitrogen atmosphere (rapid decomposition at 400°). The CS polymerization can be explosive and care must be taken so that large amounts of the monomer do not collect in specific areas of the vacuum system.

The CS monomer behaves as a weak Lewis base, not like an electrophilic carbene. It will not react at low temperatures with olefins, alcohols, and other electron-rich species but will react with Lewis acids such as boron halides, hydrogen halides, and halogens. Some Lewis acids, such as carboxylic acids and acid halides, cause delay in CS polymerization, apparently by complexation at low temperature. Also at low temperatures, CS will not displace ligands such as CO or triphenylphosphine in compounds such as nickel carbonyl, iron pentacarbonyl, or chlorotris(triphenylphosphine)rhodium(I).

### Experimental Section

Control experiments for all reactions reported showed that carbon disulfide did not react with the substrates, under the conditions employed.

All yields are based on carbon disulfide decomposed in the discharge, thus assuming each molecule of carbon disulfide leads to a molecule of CS.

The discharge apparatus consisted simply of a 40 cm × 18 mm glass tube. Connected to each end were 16 cm × 30 mm glass lengths with 24/40 ground joints. Metal electrodes were constructed so that they penetrated the discharge tube and were set 50 cm apart. The upper 24/40 joint was connected to a metering system and vacuum line for CS<sub>2</sub> inlet, while the lower 24/40 joint was connected to a three-necked round-bottom flask which in turn was connected to the vacuum system. When solution-phase reactions were carried out, a metal U trap at -196° was inserted between the flask and vacuum

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Table I. Physical Properties and Spectra of Compounds

Compd	Bp, °C (pressure, Torr)	Ir, cm <sup>-1</sup>	Nmr (CS <sub>2</sub> )	Mass spectra (major ions, 70 eV)
Cl <sub>3</sub> CSCl <sup>a</sup>	66 (50)	745 vs, 762 vs, 809 vs (neat)		P, P - Cl, CCl <sub>3</sub> , CCl <sub>2</sub> , CSCl, CCl CS, Cl, S
Br <sub>3</sub> CSBr <sup>b</sup>	65 (15) dec	753 s, 721 m, 638 vs (neat)		P, P - Br, CBr <sub>3</sub> , CSBr <sub>2</sub> , CSBr, SBr, CBr, Br, CS, S
Cl <sub>2</sub> BrCSCl	160 (740) dec	785 s, 828 m, 1150 w (gas)		P, P - Cl, CCl <sub>2</sub> Br, CSCl <sub>2</sub> , Br, SCl, CCl, S
Cl <sub>2</sub> HCSCl <sup>11,c</sup>	126 (738)	755 vs, 785 vs, 1128 w, 1161 s, 1220 s, 1265 w, 2965 w, 3000 m (neat)	Singlet, δ 6.80	P, P - Cl, CHCl <sub>2</sub> , CSH, HCl, S
Cl <sub>2</sub> HCSCHCl <sub>2</sub> <sup>11,c</sup>	72 (6) <sup>c</sup>	730 s, 765 vs, 795 vs, 1180 s, 1220 s, 1270 w, 3000 m (neat)	Singlet, δ 6.72	P, P - Cl, CHCl <sub>2</sub> , CCl <sub>2</sub> , CSCl, CSH, HCl, Cl, S
HClCS trimer	Dec	730 vs, 770 vs, 1065 m, 1150 s, 1190 vs, 1260 m, 1685 m, 2945 s (CS <sub>2</sub> smear)	Singlet, δ 6.73, 1 H; singlet, δ 6.29, 2 H (in C <sub>6</sub> D <sub>6</sub> : broad singlet, δ 6.28)	P, P - Cl, P - SCl, P - HCICS, C <sub>2</sub> HS <sub>2</sub> Cl <sub>2</sub> , C <sub>2</sub> HSCl, HCICS, CHS <sub>2</sub> , CS <sub>2</sub> , S <sub>2</sub> , CCl, CSH, CS, HCl, Cl, CS
HBrCS trimer	Dec	730 vs, 750 vs, 1120 vs, 1155 vs, 1260 m, 1690 m, 2940 m, 2980 m (CS <sub>2</sub> smear)	Singlet, δ 6.82, 2 H; singlet, δ 6.55, 1.2 H; singlet, δ 6.47, 1 H (in C <sub>6</sub> D <sub>6</sub> : broad singlet, δ 6.12)	P - CS, P - HCS, P - Br, P - HBrCS, C <sub>2</sub> HS <sub>2</sub> Br <sub>2</sub> , C <sub>2</sub> H <sub>3</sub> - SBr, C <sub>2</sub> H <sub>2</sub> S <sub>2</sub> Br, HBrCS, HBr, Br, CS <sub>2</sub> , S <sub>2</sub> , CSH, CS, S

<sup>a</sup> "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1951, p 506. <sup>b</sup> E. Kuehle, E. Klauke, and F. Greive, *Angew. Chem.*, 76, 807 (1964). <sup>c</sup> I. B. Douglass, F. T. Martin, and R. Addor, *J. Org. Chem.*, 16, 1297 (1951).

system. This trap served as a safe polymerization site for CS escaping the reactor flask. The discharge was set up by connecting the electrodes to an ac luminous tube transformer (12,000 V, 60 mA, Jefferson Electric Co., Catalog No. 721-421) and adjusting the power input with a normal Variac. Depending on power input, up to 75% of the CS<sub>2</sub> was decomposed, but usually the setting was for 25% decomposition (as determined by numerous control experiments) since fewer problems with violent CS polymerizations were encountered at this setting. Normally about 3-5 g of carbon disulfide was metered through the discharge in about 0.5 hr, and the discharge effluent was swept into the reactor flask which was open to the vacuum system. Both codeposition and solution-phase experiments were carried out.

**Codeposition Experiments.** For codeposition experiments a 1-l. round-bottom reactor flask immersed in liquid nitrogen was used. A fivefold excess of substrate to CS was cocondensed throughout the flask with the CS-CS<sub>2</sub> effluent in a period of about 30 min. The matrix usually turned color on slight warming and was allowed to warm to near room temperature. Then products were separated by conventional vacuum-line techniques. Nonvolatile products were washed out of the reactor with carbon disulfide solvent.

**CS + BrCl.** In a 2-l. bulb were placed 1.70 g of chlorine (0.024 mol) and 3.90 g of bromine (0.024 mol). This mixture was degassed and allowed to stand several days forming an equilibrium mixture of Cl<sub>2</sub>, Br<sub>2</sub>, and BrCl. This gas mixture was codeposited with CS-CS<sub>2</sub> discharge effluent (3.0 g of CS<sub>2</sub>, 0.040 mol, or with 25% decomposition, 0.010 mol of CS) at -196°. After deposition the reactor contents were allowed to warm slowly to room temperature without pumping, then cooled to -196° again, and slowly allowed to warm while pumping through cold traps at -78 and -196°. The reactor residue was washed out with CS<sub>2</sub>, but only polymeric material was recovered in this fraction. The -196° trap contained CS<sub>2</sub>, Br<sub>2</sub>, Cl<sub>2</sub>, and BrCl. The -78° trap contained all the volatile CS products, and this was subjected to glpc analysis on a silicone rubber SE 30 5 ft × 1/4 in. 20% column (oven 100°, injector 100°). Thus yields based on CS<sub>2</sub> decomposed were 15% CBr<sub>3</sub>CBr, 38% CCl<sub>2</sub>CCl, and 27% Cl<sub>2</sub>BrCSCl. Pure samples of these materials were collected by preparative glpc (see Table I for physical properties and spectra).

**CS + Cl<sub>2</sub>; CS + Br<sub>2</sub>; CS + ICl.** The general procedure above was followed with Cl<sub>2</sub> yielding Cl<sub>3</sub>CSCl (55%). For Br<sub>2</sub> some of the Br<sub>3</sub>CBr remained in the reactor after pumpoff and was washed out with CS<sub>2</sub>. The washings and -78° trap together yielded Br<sub>3</sub>CSBr in 45% yield. For ICl apparently much halogen exchange took place and Cl<sub>3</sub>CSCl was obtained in the -78° trap in 67% yield. Iodine and ICl were also found in the -78° trap which made separation of the Cl<sub>3</sub>CSCl very difficult. The yield of this material was determined by glpc.

**CS + HCl; CS + HBr.** The general procedure above was followed. The nonvolatile HCIC=S trimer was washed out of the reactor with CS<sub>2</sub>, the red-brown solution filtered, and the CS<sub>2</sub> rotovaced off leaving

the reddish oil (HCICS)<sub>3</sub> in about 50% yield. Similarly the (HBrCS)<sub>3</sub> was obtained as a red, air-sensitive oil in about 75% yield. [These yields are based on (moles of CS)/3.]

**CS + HCl (Cl<sub>2</sub>).** In a 2-l. bulb were placed HCl (0.06 mol) and Cl<sub>2</sub> (0.006 mol) (10:1 ratio of HCl:Cl<sub>2</sub>), and this mixture was degassed and allowed to stand several days. Then codeposition with CS-CS<sub>2</sub> discharge effluent (2.8 g of CS<sub>2</sub>, 0.037 mol, or with 25% decomposition, 0.0092 mol of CS) was carried out in 20 min. The reactor contents were allowed to warm to about -10° without pumping, then cooled to -196° again, opened to the vacuum system again, and pumped through traps at -78, -116, and -196°. The reactor residue was washed out with CS<sub>2</sub> to yield a very small portion of (HCICS)<sub>3</sub>. The -196° trap contained HCl and Cl<sub>2</sub>, and the -116° trap contained CS<sub>2</sub>. The -78° trap contained CS products and was analyzed by glpc as in the section on CS + BrCl. Two major products were found, isolated by preparative glpc, and shown to be HCl<sub>2</sub>CSCl (26%) and Cl<sub>3</sub>CSCl (14%).

**CS + HCl Followed by Cl<sub>2</sub> Addition.** Codeposition of HCl and CS-CS<sub>2</sub> discharge effluent was carried out. The reactor was allowed to warm to room temperature without pumping, cooled to -196° again, and allowed to warm while the HCl and CS<sub>2</sub> were pumped off. Then an excess of Cl<sub>2</sub> was condensed in at -196°, and the mixture brought to room temperature and held for 35 min. The dark red-brown (HCICS)<sub>3</sub> reacted to form a dark liquid. Elemental sulfur present also reacted. The reactor contents were pumped through traps at -78, -116, and -196°. The -196° trap contained Cl<sub>2</sub>, the -116° trap contained S<sub>2</sub>Cl<sub>2</sub> (from S + Cl<sub>2</sub> reaction), and the -78° trap contained mainly HCl<sub>2</sub>CSCl (20%) and HCl<sub>2</sub>CSCCl<sub>2</sub>H (26%). When the same experiment was carried out without having pumped off the excess HCl, the yields were 31 and 23%, respectively, based simply on CS<sub>2</sub> decomposed.

**Solution-Phase Experiments.** For solution-phase experiments a 250-cm<sup>3</sup> reactor flask was charged with a magnetic stirring bar, 100 ml of solvent, and an excess of substrate. A reaction temperature was chosen so that the mixture remained liquid but had a very low vapor pressure so that the discharge could be operated at low pressure. The CS-CS<sub>2</sub> effluent was swept down onto the surface of the stirred mixture and was taken up very efficiently by reactive substrates, *i.e.*, bromine (64 g, 0.40 mol) in chloroform (100 ml) at -72°. Over a 3-hr period the carbon disulfide (9.0 g, 0.12 mol, 25% decomposition to 0.03 mol of CS) was inhaled. Upon fractional distillation of the product mixture, some tribromosulfonyl bromide (CSBr<sub>3</sub>) decomposed, but 5 g (47% based on carbon disulfide decomposed) was isolated [bp 65° (15 mm)] (see Table I for spectroscopic data).

**Acknowledgment.** We thank the National Science Foundation (Grant GP-34493) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No.  $\text{Cl}_2\text{CSCl}$ , 594-42-3;  $\text{Br}_2\text{CSBr}$ , 993-30-6;  $\text{Cl}_2\text{BrCSCl}$ , 51174-92-6;  $\text{Cl}_2\text{HCSCl}$ , 42172-24-7;  $\text{Cl}_2\text{HCSCHCl}_2$ , 51174-93-7;  $\text{HCl-CS}$  trimer, 51174-94-8;  $\text{HBrCS}$  trimer, 51174-95-9;  $\text{CS}$ , 2944-05-0.

Contribution from the Department of Chemistry,  
University of Minnesota, Minneapolis, Minnesota 55455

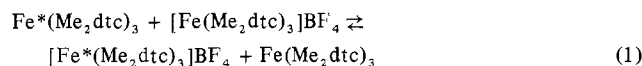
### Rate of Electron Transfer between Tris(dithiocarbamate) Complexes of Iron(III) and Iron(IV) by Proton Magnetic Resonance<sup>1</sup>

M. C. Palazzotto and L. H. Pignolet\*

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The rate of the electron-transfer reaction, eq 1, between



tris(*N,N*-dimethyldithiocarbamate)iron(III),  $\text{Fe}(\text{Me}_2\text{dtc})_3$ , and tris(*N,N*-dimethyldithiocarbamate)iron(IV) tetrafluoroborate,  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$ , has been measured by pmr line-broadening techniques in  $\text{CD}_2\text{Cl}_2$  solution. Reaction 1 is ideally suited for a pmr kinetic investigation of electron transfer because the *N*- $\text{CH}_3$  resonances of the iron(III) and -(IV) species are well separated (before mixing) with a chemical shift difference of 111 ppm at  $-91^\circ$ . This large separation, which permits the measurement of rates of very fast reactions (second-order rate constants of *ca.*  $10^8$  l. mol<sup>-1</sup> sec<sup>-1</sup>) results from the difference in paramagnetism of the iron(III) and iron(IV) complexes.<sup>2,3</sup>

A mixture of  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$  in  $\text{CD}_2\text{-Cl}_2$  solution shows one *N*- $\text{CH}_3$  resonance at  $30^\circ$  which is a weighted average of the iron(III) and -(IV) *N*- $\text{CH}_3$  positions. As the temperature is lowered, the averaged *N*- $\text{CH}_3$  resonance broadens more rapidly than predicted from spectra of the unmixed complexes<sup>4</sup> and at *ca.*  $-91^\circ$  broadens almost to the base line (see Figure 1). Over this temperature range the *N*-methyl resonances in the unmixed complexes remain sharp with line widths at half-height at  $-91^\circ$  of 46 and 35 Hz for iron(III) and -(IV), respectively,<sup>2</sup> while a value of 1700 Hz is found for the mixture. The averaging and kinetic broadening result from electron exchange as shown in reaction 1. The observation of exchange broadening due to electron transfer in a mixture of these complexes has not previously been reported.<sup>1</sup> This is the first report of electron transfer between dithiocarbamate complexes and indeed between any complexes of iron(III) and -(IV).

Kinetic parameters for electron transfer were determined by a total line shape analysis of the exchange-broadened *N*- $\text{CH}_3$  resonance. The Binsch CLATUX computer program, which employs the modified Bloch equations and allows unequal nonexchanging line widths, was used.<sup>5</sup> The best fit line shapes are shown with dashed lines above the experi-

Table I. Pmr Data<sup>a</sup> and Rate Constants for Electron Transfer between  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$

Temp, °C (±1°)	$10^{-8}k_2$ , <sup>b</sup> l. mol <sup>-1</sup> sec <sup>-1</sup>	$\Delta\nu$ , <sup>c</sup> ppm	$H_{1/2}$ , <sup>d</sup> Hz	
			Fe(III)	Fe(IV)
-32	2.5 ± 0.2	35.94	46	13.5
-38	2.4 ± 0.2	40.26	46	14.5
-45	2.1 ± 0.1	45.61	46	16.0
-50	1.6 ± 0.1	49.63	46	17.0
-56	1.3 ± 0.1	54.68	46	18.8
-62	1.1 ± 0.1	60.04	46	20.5
-69	1.0 ± 0.1	66.69	46	23.0
-73	0.83 ± 0.1	70.69	46	25.0
-81	0.68 ± 0.1	79.20	46	28.0

<sup>a</sup> *N*- $\text{CH}_3$  resonance recorded at 100 MHz using  $\text{CD}_2\text{Cl}_2$  solvent. Complex concentrations for Fe(III) and Fe(IV) are  $2.45 \times 10^{-3}$  and  $1.63 \times 10^{-3}$  M, respectively, at  $25^\circ$ . Density corrections were applied for the other temperatures. <sup>b</sup> Errors in  $k_2$  are estimated using errors in concentration (~10%) and the visual line shape fit which includes the errors in  $\Delta\nu$  and  $H_{1/2}$ . <sup>c</sup> Chemical shift separations between Fe(III) and Fe(IV). Error is estimated to be ±0.1 ppm. <sup>d</sup> Line width at half-height. Error is estimated to be ±0.5 Hz.

mental spectra in Figure 1 at several temperatures. The rate constants,  $k$ , shown in this figure are pseudo first order and represent the quantity  $k_2[\text{III}]$  in

$$\text{rate} = k_2[\text{III}][\text{IV}]$$

where III and IV are the iron(III) and -(IV) complexes, respectively. Therefore the reciprocal of  $k$  equals the lifetime of the iron(IV) complex. A concentration study at  $-57^\circ$  shows that the reaction is second order overall with  $k_2 = (1.5 \pm 0.4) \times 10^8$  l. mol<sup>-1</sup> sec<sup>-1</sup> in good agreement with the variable-temperature data ( $k_2(-57^\circ) = (1.4 \pm 0.1) \times 10^8$  calculated from a least-squares fit, Figure 2). The data used in the line shape fit and the second-order rate constants,  $k_2$ , are listed in Table I. Figure 2 shows the Eyring plot of  $\ln k_2/T$  vs.  $1/T$  for the variable-temperature rate data. The chemical shift difference between the Fe(III) and Fe(IV) species,  $\Delta\nu$ , and the line widths at half-height,  $H_{1/2}$ , for the nonexchanging complexes are directly observed at each temperature and are listed in Table I. No extrapolation is required. Activation parameters were determined from the Eyring plot by a linear least-squares fit. The enthalpy and entropy of activation are  $\Delta H^\ddagger = 2.1 \pm 0.4$  kcal/mol and  $\Delta S^\ddagger = -11 \pm 4$  eu. Errors were estimated by drawing the maximum and minimum sloped lines within the error bars on the Eyring plot. The error bars come from errors listed in Table I.

The temperature dependence of the chemical shift separation needs some mention. As can be seen in Table I,  $\Delta\nu$  greatly increases with decreasing temperature. This phenomenon is unusual and results because the *N*- $\text{CH}_3$  resonance position of the Fe(III) complex shows non-Curie temperature dependence due to the presence of an  $S = 1/2 \rightleftharpoons S = 5/2$  spin state equilibrium (*vide infra*).<sup>2</sup> The Fe(IV) complex is low spin,  $S = 1$ , and is magnetically well behaved.<sup>2</sup>

Numerous electron-transfer reactions have been studied,<sup>6</sup> however, only a few by nmr line-broadening techniques.<sup>7-9</sup>

(6) See for example the following references: (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 6; (b) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 303 (1972); (c) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966; (d) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

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(4) In the absence of exchange broadening (*i.e.*, in the fast-exchange limit) the averaged line width is simply a weighted average of the nonexchanging resonance widths.

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