to ΔS^0 of the CN^-. Thus, the observed ΔS^0 is essentially that resulting from the contribution of the proton. The molecules previously studied by Canady, *et al.*, and by us had low polarity and, thus, did not show this effect to an appreciable extent.

CONTRIBUTION FROM THE INSTITUTE FOR PHYSICAL CHEMISTRY,
UNIVERSITY OF COPENHAGEN, DENMARK, AND THE
DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK

The Electronic Structures and Magnetic Properties of the Chromyl and Molybdenyl Ions

BY CURTIS R. HARE, IVAN BERNAL, AND HARRY B. GRAY

Received April 19, 1962

The electron spin resonance spectra and the magnetic susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ are reported. The results are consistent with an electronic structural description which includes considerable oxygen-to-metal π-bonding. Complete consistency between the e.s.r. and the susceptibility data is found for $(NH_4)_2[MoOCl_5]$. The lack of consistency of the data for $Rb_2[CrOCl_5]$ is attributed to the presence of a small amount of Cr^{3+} impurity. Comparison of e.s.r. data with reported susceptibility data for Mo^{5+} solutions of varying HCl concentration is interpreted in terms of the nature of the species present.

Introduction

In a previous report[1] the electronic structures and spectra of the chromyl (CrO^{3+}) and molybdenyl (MoO^{3+}) ions were discussed. Both the charge transfer and the "crystal field" d-d spectra could be accounted for by the molecular orbital energy level scheme derived for the electronically equivalent (d^1) vanadyl (VO^{2+}) ion.[2] The most striking feature of the electronic structures of these oxycations is the existence of considerable oxygen-to-metal π-bonding.

In the present paper the electron spin resonance spectra and the temperature dependencies of the magnetic susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ are investigated and the results are interpreted in terms of the previously proposed electronic structural description. The magnetic susceptibilities of solid samples of $(NH_4)_2[MoOCl_5]$[3] and $Rb_2[CrOCl_5]$[4] and solutions of Mo^{5+} [5] have been reported in the literature, but for only room temperature.

A comparison of the results of the present e.s.r. measurements on Mo^{5+} solutions with the susceptibility results of Sacconi and Cini[5] allows an interpretation of the magnetic nature of the species present in these solutions.

Results

Chromyl Ion.—The electron spin resonance spectrum of a solid sample of $Rb_2[CrOCl_5]$ shows a single broad resonance line centered at $g = 1.986$. The g value indicates an orbitally nondegenerate ground state, as expected for a compound containing CrO^{3+}. The g factor for a paramagnetic molecule with an orbitally nondegenerate ground state differs from 2.0023 due to the mixing of ground state and excited states *via* spin-orbit coupling. The expressions for the g values for d^1 transition metal oxycations in C_{4v} ligand fields are[2]

$$g_{\perp} = 2.0023\left(1 - \frac{\xi}{\Delta E(^2B_2 \longrightarrow {}^2E(I))}\right) \quad (1)$$

$$g_{\parallel} = 2.0023\left(1 - \frac{4\xi}{\Delta E(^2B_2 \longrightarrow {}^2B_1)}\right) \quad (2)$$

with

$$\langle g\rangle^2 = 1/3\,(2g_{\perp}^2 + g_{\parallel}^2) \quad (3)$$

In these equations ξ is the spin-orbit coupling constant for Cr^{5+} in CrO^{3+} and the ΔE's are the energies of known crystal field transitions in $Rb_2[CrOCl_5]$.[1] The ξ value for CrO^{3+} is calculated to be 65 cm.$^{-1}$, using the observed $\langle g\rangle$ value and the known ΔE values ($\Delta E(^2B_2 \rightarrow {}^2E(I)) = 12{,}900$ cm.$^{-1}$, $\Delta E(^2B_2 \rightarrow {}^2B_1) = 23{,}500$ cm.$^{-1}$).

---

[1] H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

[2] C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

[3] B. T. Tjabbes, *Proc. Acad. Sci. Amsterdam*, **35**, 693 (1932); *Chem. Abstr.*, **26**, 4987 (1932).

[4] R. W. Asmussen, "Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Gjellerups Forlag, Copenhagen, 1944.

[5] L. Sacconi and R. Cini, *J. Am. Chem. Soc.*, **76**, 4239 (1954).

The predicted values of $g_\perp$ and $g_\parallel$ are, respectively, 1.990 and 1.978.

The magnetic susceptibility of $Rb_2[CrOCl_5]$ was measured over the range 77–318°K. These diamagnetic corrected data are given in Table I. The theoretical expression for magnetic susceptibility given by Van Vleck[6] is

$$\chi = (C/T) + \chi_{\text{H.F.}} \qquad (4)$$

where C is the Curie constant and $\chi_{\text{H.F.}}$ is the temperature-independent contribution to the susceptibility. In this case

$$C = N\beta^2\langle g\rangle^2/4k \qquad (5)$$

where N is Avogadro's Number, β is the Bohr magneton, k is Boltzmann's constant, and

$$\chi_{\text{H.F.}} = \frac{2N\beta^2}{g_m}\left[\frac{2}{3}\sum_i \frac{|<\psi_0|L_x + 2S_x|\psi_i>|^2}{\Delta E_{0,i}} + \frac{1}{3}\sum_i \frac{|\psi_0|L_z + 2S_z|\psi_i>|^2}{\Delta E_{0,i}}\right] \qquad (6)$$

where $\Delta E_{0,i}$ represents the energy differences from the ground state ψ_0 to excited states ψ_i.

For $Rb_2[CrOCl_5]$, with $\langle g\rangle = 1.986$ and ΔE's from the spectral data, eq. 4 gives

$$\chi = (0.370/T) + 55 \times 10^{-6} \qquad (7)$$

A plot of χ *vs.* $(1/T)$ for $Rb_2[CrOCl_5]$ is shown in Fig. 1. This plot gives

$$\chi = 0.536/T \qquad (8)$$

in very poor agreement with the calculated equation. The compound is unstable, and even at room temperature decomposition to give Cr^{3+} and Cr^{6+} takes place; total decomposition occurs above 45°. While care was taken to reduce handling times and to protect the samples from oxidative conditions and moisture, it is probable that some decomposition did take place. A rough correction was applied to the data to account for the susceptibility of Cr^{3+} impurity. It was found that a 7% impurity of Cr^{3+} would account for the deviations from the expected behavior. This correction is only possible because the effective magnetic moment of the impurity does not vary with temperature.[7] Further refinement of the data is not justified.

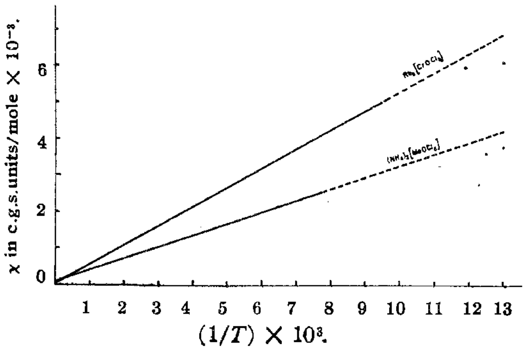


Fig. 1.—Magnetic susceptibilities of $Rb_2[CrOCl_5]$ and $(NH_4)_2[MoOCl_5)$ *vs.* $1/T$. All experimental points fall on the lines except as indicated.

Table I

Magnetic Susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$

$(NH_4)_2[MoOCl_5]$ diamagnetic correction, 153.9×10^{-6}		$Rb_2[CrOCl_5]$ diamagnetic correction, 165.3×10^{-6}	
°K.	χ'_M[a]	°K.	χ'_M[a]
77	3742	77	6065
80	3619	84	5930
129	2519	145	3741
189	1777	152	3524
195	1754	159	3420
201	1706	164	3258
206	1654	170	3141
212	1605	177	3046
217	1556	183	2958
223	1530	189	2792
228	1514	195	2738
233	1484	201	2650
238	1455	206	2571
243	1416	212	2517
248	1374	217	2442
255	1348	223	2375
261	1325	228	2309
267	1299	233	2246
273	1273	238	2209
295	1195	243	2192
306	1169	248	2142
333	1075	255	2113
375	958	261	2030
424	853	267	1984
471	766	273	1934
		294	1797
		301	1797
		308	1772
		318	1726

[a] χ'_M is the molar susceptibility in units $\times 10^{-6}$ c.g.s./mole corrected for diamagnetism.

Molybdenyl Ion.—Detailed spectral studies[1,8,9] have shown that the ion $MoOCl_5^{2-}$ is present as a monomer in 10–12 M HCl solutions of $(NH_4)_2[MoOCl_5]$. The electron spin resonance spectrum of MoO^{3+} in 10–12 M HCl shows a strong central line centered at $g = 1.947$. The central line is flanked by three weak satellites on each side. The strong central line is due to the $^{96}Mo(I = 0$; abundance, 74.82%) isotope; the weaker

---

(6) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Orford University Press, 1932.

(7) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 3138 (1961).

(8) C. K. Jorgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

(9) G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, in press.

satellites are due to the ^{95}Mo($I = {}^5/_2$; abundance, 15.78%) and ^{97}Mo ($I = {}^5/_2$; abundance, 9.6%) isotopes. The latter two isotopes have approximately the same nuclear moment and thus the six weak satellites were not resolved into hyperfine contributions due to the individual isotopes. The average hyperfine splitting due to the ^{95}Mo and ^{97}Mo isotopes is about 50 gauss.

The intensity of the e.s.r. spectrum of a MoO^{3+} solution decreases drastically going from 10 to 4 *M* HCl; at 4 *M* HCl the e.s.r. signal is barely detectable. It is also important to note that the width of the central line stays constant at about 8 gauss, independent of the HCl concentration. The percentage of MoO^{3+} monomer present in solution at the various HCl concentrations is directly proportional to the intensity of the e.s.r. spectrum. The analysis of these e.s.r. intensities in terms of the percentage of MoO^{3+} monomer present is given in Table II.

TABLE II

Concentration of HCl, *M*	% total susceptibility[a]	% MoO^{3+} monomer from e.s.r. results	Difference
12	100	100	0
10	100	100	0
8.4	99	85	14
7.1	95	74	21
6	75	46	29
5.2	41	16	25
4	9	about 1	8
2	0	0	0

[a] From the data of Sacconi and Cini (see ref. 5).

For the $MoOCl_5^{2-}$ monomer, with $\langle g \rangle = 1.947$, $\Delta E(^2B_2 \rightarrow {}^2E(I)) = 13{,}800$ cm.$^{-1}$, and $\Delta E(^2B_2 \rightarrow {}^2B_1) = 23{,}000$ cm.$^{-1}$, the spin–orbit constant, $g_{\parallel}$, and $g_{\perp}$ can be obtained from eq. 1, 2, and 3. This calculation gives $g_{\perp} = 1.965$, $g_{\parallel} = 1.915$, and $\xi = 240$ cm.$^{-1}$.

The magnetic susceptibility of a solid sample of $(NH_4)_2[MoOCl_5]$ was measured between 77 and 470°K. These results are given in Table I. For $(NH_4)_2[MoOCl_5]$, with $\langle g \rangle = 1.947$ and the ΔE's from the spectral data,[1] eq. 4 becomes

$$\chi = (0.356/T) + 55 \times 10^{-6} \qquad (9)$$

A plot of χ *vs.* $1/T$ is shown in Fig. 2. The linear portion of this curve gives $C = 0.333$ and $\chi_{\text{H.F.}} = 90 \times 10^{-6}$, in satisfactory agreement with the predicted equation (9).

Equation 9 does not account for the "tailing off" of the χ *vs.* $1/T$ curve at low temperatures. This non-linearity may be accounted for by including the Weiss constant in the temperature dependent term of eq. 9. This more detailed analysis of the experimental susceptibility results gives the expression

$$\chi = 0.35/(T + 15) + 75 \times 10^{-6} \qquad (10)$$

which is in excellent agreement with theory. The average effective moment corrected for the temperature independent paramagnetism is found to be 1.67 B.M., which of course is expected, since $\mu^2 = {}^3/_4 \langle g \rangle^2$. The small θ value of +15°K. may be due to a small degree of antiferromagnetism ($J = 4$°K.) or a lack of magnetic dilution.

Discussion

The electronic structural similarities of VO^{2+}, CrO^{3+}, and MoO^{3+}, concluded from detailed spectral studies, already have been elaborated.[1] The existence of considerable oxygen-to-metal π-bonding seems to be the principal feature of the electronic structure of these d^1 oxycations.

The magnetic properties of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ are completely consistent with this electronic structural description. The $\langle g \rangle$ values are very nearly 2, indicating that the orbital angular momentum is effectively quenched in the low symmetry ligand field. The free ion spin-orbit coupling constants for Cr^{5+} (380 cm.$^{-1}$) and Mo^{5+} (1030 cm.$^{-1}$)[10] are drastically reduced in the oxycations; for CrO^{3+}, $\xi = 65$ cm.$^{-1}$; for MoO^{3+}, $\xi = 240$ cm.$^{-1}$. This reduction in ξ also is observed for VO^{2+} and is accounted for by the oxygen-to-metal π-bonding.[2]

The structures of Mo^{5+} species in solutions of varying HCl concentration deserve special attention. It may be safely concluded from previous spectral studies and the present e.s.r. investigation that the monomer MoO^{3+} is the only species present in 10–12 *M* HCl solutions. The situation is more complicated in solutions less than 10 *M* in HCl. There are now three different types of information available on these solutions; (1) the magnetic susceptibility results reported by Sacconi and Cini,[5] (2) the electronic spectral results reported by Haight,[9] and (3) the present e.s.r. investigation. The bulk magnetic susceptibility measurements represent all the paramagnetic species in solution. The e.s.r. experiments are able to give just the amount of MoO^{3+} monomer present at any given HCl concentration. Table II affords a comparison of the magnetic

---

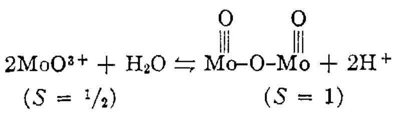
(10) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

susceptibility and the e.s.r. results for Mo^{5+} solutions.

Haight[9] has concluded that both a paramagnetic and a diamagnetic dimer are formed in solutions where the HCl concentration is lower than 10 *M*. It is significant that, as the HCl concentration decreases, the amount of MoO^{3+} monomer in solution disappears much more rapidly than would be expected from the total paramagnetic susceptibility of the solution. This must mean that there is another paramagnetic species in solution in the 4–10 *M* HCl region. The amount of this other paramagnetic species is proportional to the difference in the magnetic susceptibility and the e.s.r. results. A plot of this "difference" *vs.* HCl concentration is shown in Fig. 2.

Three different regions are clearly discernible in Fig. 2. In the first region, between 12 and 10 *M* HCl, the static susceptibility and e.s.r. data give the same results. In this region only the monomer MoO^{3+} is present. In the second region, between 10 and 2 *M* HCl, there is a difference in the magnetic susceptibility and the e.s.r. results. This difference reaches a maximum value at about 6 *M* HCl, and then decreases steadily until the HCl concentration reaches 2 *M*; at 2 *M* HCl and below, the third region, both magnetic measurements indicate no paramagnetic species in solution.

Consider now the first part (10 to 6 *M* HCl) of the second region; the experimental observations here are consistent with the formation of a paramagnetic dimer



$$2MoO^{3+} + H_2O \rightleftharpoons \overset{\overset{\displaystyle O}{|||}}{Mo}\text{–O–}\overset{\overset{\displaystyle O}{|||}}{Mo} + 2H^+ \qquad (11)$$
$$(S = 1/2) \qquad\qquad (S = 1)$$

When two species with $S = 1/2$ are coupled to form a dimer with $S = 1$, the spin-only moment of the dimer is about 82% of that due to two monomeric species. Thus the data of Sacconi and Cini[5] in the 10 to 6 *M* HCl region can be explained by assuming that most of the decrease in magnetic moment is due to such dimer formation.

The spectral studies carried out by Haight[9] give a strong clue as to the structure of this paramagnetic dimer. The only spectral band of $MoOCl_5^{2-}$ which is markedly affected by the dimerization is the band assigned to the $^2B_2 \rightarrow {}^2B_1$ transition. *This transition is in turn the only electronic transition localized in the plane perpendicular to the MoO^{3+} axis.*[1] Therefore it is reasonable to formulate the dimer as bridged by an atom in the *x*, *y* plane. The known pH dependence[9] of the equilibrium in eq. 11 further suggests that the bridging atom is a water oxygen, freed of its two protons during the bridging process.

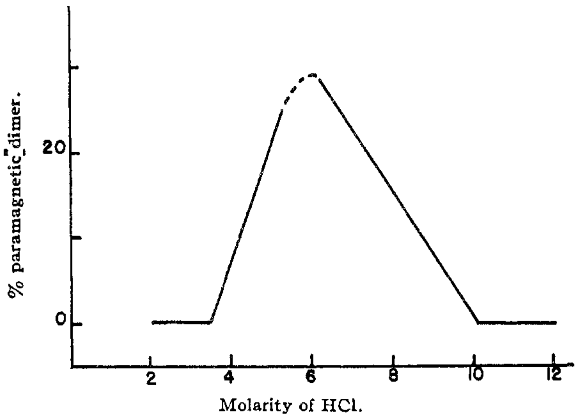


Fig. 2.—The percentage of the paramagnetic dimer of MoO^{3+} at various HCl concentrations indicated from a comparison of magnetic susceptibility and e.s.r. measurements.

The rate of attainment of equilibrium between the MoO^{3+} monomer and the paramagnetic dimer must be slow due to bond rearrangements. This is shown by the fact that the width of the central e.s.r. line is constant at all HCl concentrations. Thus the rate of exchange must be much smaller than 10^8 sec.$^{-1}$ This is an important result, since it means that the paramagnetic dimer is not a species formed by weak interaction between two MoO^{3+} monomers. If this had been the case, the central e.s.r. line would have been broadened out as the HCl concentration decreased.

In the second part of the second region, between 6 and 2 *M* HCl, the paramagnetic dimer begins to disappear rapidly, forming some diamagnetic species. It is interesting to note that at 4 *M* HCl there is no MoO^{3+} monomer left in solution, and only paramagnetic dimer contributes to the paramagnetic susceptibility. In the third region, below 2 *M* HCl, only diamagnetic species are present.

Experimental

(1) **Preparation of Compounds.**—The compounds used in this work were prepared by the methods described in the previous paper.[1]

(2) **Electron Spin Resonance Measurements.**—The electron spin resonance measurements were carried out in a spectrometer described by Fraenkel and co-workers.[11] The spectrum of $Rb_2[CrOCl_5]$ was measured on a powdered

---

[11] J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955); H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.*, to be published.

sample sealed in a 3-mm. tube under nitrogen. The solutions used for the measurement of the spectrum of $(NH_4)_2[MoOCl_5]$ were 0.03 *M*. It was noted that the line width of this compound does not change on dilution to 0.003 *M*, therefore the more concentrated solution was chosen to obtain a stronger signal. The strength of a given line was measured by the area under the curve. All e.s.r. measurements were made at 19 ± 1°. The magnetic susceptibility measurements of Sacconi and Cini[5] on MoO^{3+} solutions were made at 20°.

(3) **Magnetic Susceptibilities.**—The magnetic susceptibility measurements were carried out on a Gouy balance using an electromagnet with a maximum field strength of about 3000 gauss. The balance was fitted with a suitable dewar flask to contain the cooling liquids. Temperatures between 77 and 273°K. were achieved by using precooled isopentane and allowing it to warm up slowly.

Acknowledgments.—The authors wish to thank Professor C. J. Ballhausen for his continued interest in this work, Professor G. P. Haight, Jr., for several helpful suggestions, and Professor G. K. Fraenkel for the use of an electron resonance spectrometer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

The Structure of the Diammoniate of Dimethylgallium Chloride, $(CH_3)_2ClGa \cdot 2NH_3$, and of Ethylenediamine–Dimethylgallium Chloride

BY DUWARD F. SHRIVER AND ROBERT W. PARRY

Received April 6, 1962

Chemical evidence supports the structure $[(CH_3)_2Ga(NH_3)_2]Cl$ for the known compound $(CH_3)_2GaCl \cdot 2NH_3$ reported by Kraus and Toonder and the structure $[(CH_3)_2Ga(H_2NCH_2CH_2NH_2)]Cl$ for the new ethylenediamine analog. The latter compound is stable in water for limited periods of time.

The compound $(CH_3)_2GaCl \cdot 2NH_3$ was reported by Kraus and Toonder[1] in 1933, but the structure was never established. An ammonium model, analogous to the early ammonia model used for the diammoniate of diborane, was suggested by Coates[2]: $[NH_4^+][(CH_3)_2GaNH_2Cl^-]$; however, little real structural evidence was ever available. Following recognition of the formula $[H_2B(NH_3)_2][BH_4]$ for the diammoniate of diborane,[3] another possible structure for the diammoniate of dimethylgallium chloride appeared probable: $[(CH_3)_2Ga(NH_3)_2]Cl$. Chemical evidence supports this latter model.

Experimental

General Procedures.—Standard vacuum line techniques were used with moisture- and oxygen-sensitive materials.[4] Filtration of air-sensitive materials was performed with the vacuum line filtration assembly which is described elsewhere.[5]

X-Ray powder patterns were obtained in 5.7 and 11.4 cm. diameter cameras with CuKα radiation. Films were read on a North American Philips film reader and intensities were estimated visually. Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam recording spectrophotometer with NaCl optics; KCl disk and Nujol mull techniques were employed. Calibration of the spectrometer was checked with indene.[6]

Materials. 1. $Ga(CH_3)_3$ was prepared by the action of 67.8 g. of $Hg(CH_3)_2$ on 13.22 g. of Ga metal (99.99% pure) in the presence of a trace of mercuric chloride. Reaction took place in a sealed glass pressure tube at 130° over a period of 9 days.[7] The $Hg(CH_3)_2$ was prepared by the method of Marvel and Gould.[8] Three fractionations of the crude $Ga(CH_3)_3$ from a vacuum trap at room temperature, through a trap at 0°, and into a trap at −78° gave a product with a vapor pressure of 65.4 mm. at 0°. This compares well with the literature values of 66.6,[7] 64.5,[9] and 65.9 mm.[1] The yield was nearly quanti-

---

(1) C. A. Kraus and F. E. Toonder, *Proc. Natl. Acad. Sci. U. S.*, **19**, 292 (1933).

(2) G. E. Coates, "Organo Metallic Compounds," Methuen and Co., Ltd., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 147.

(3) S. G. Shore, D. R. Schultz, R. W. Parry, *et al.*, *J. Am. Chem. Soc.*, **80**, 1–29 (1958).

(4) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.

(5) R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 2 (1958).

(6) R. N. Jones, P. K. Faure, and W. Zaharias, *Rev. Universelle Mines*, **15**, 417 (1959).

(7) E. Wiberg, T. Johannsen, and O. Stecher, *Z. anorg. Chem.*, **251**, 114 (1943).

(8) C. S. Marvel and V. L. Gould, *J. Am. Chem. Soc.*, **44**, 153 (1922).

(9) T. Wartik and H. I. Schlesinger, *ibid.*, **75**, 835 (1953).